Interfacial adhesion performance between the low-density polyethylene (LDPE) modified bitumen and minerals based on molecular dynamics simulations

By

Huajie Guo (SUN:159229495)

A THESIS

Aston University

Under the Supervision of Professor. Yuqing Zhang

January 31, 2021

ABSTRACT

Since the first plastic scale production, plastic consumption has amplified from 5 million tonnes to 322 million tonnes per year. Correspondingly, plastic waste has increased substantially and is now associated with detrimental effects to humans and wildlife. Therefore, plastic waste is a shared interest of exploration for many researchers as they all hold a common goal to look for safe and sustainable alternative solutions.

Many scientists found that the incorporation of waste plastic such as low-density polyethylene (LDPE) can potentially improve the rheological performance and high temperature performance of bitumen. However, the LDPE modified asphalt binder has frequently encountered the adhesive failures resulting from the adhesion loss at the bitumen-aggregate interface, particularly when subjected to the oxidative ageing conditions. Adhesion is defined as the molecular force of attraction in the area of contact between the adhesive materials and substrates. A series studies have been used experiment tests to evaluate adhesion property of the asphalt binder. Although these studies have provided meaningful and progressive insights, it is still necessary for further exploration to better understand the microstructure and physical properties of asphalt binder, particularly when the plastic is incorporated in the binder. However, rat the current stage, the research on adhesion of asphalt binder is limited and there is no established technique which can be used to quantify the adhesive bond strength between the minerals and LDPE modified bitumen at microscale.

Only in the past 5 years, some researchers used molecular dynamic (MD) simulations to analyze the effect of oxidative aging on the adhesion performance of asphalt pavement. This is because MD simulation can simulate physical movements of atoms and molecules following Newton's

second law, which is advantageous than traditional experiment and numerical computation in understanding the molecular scale behaviors. Literature search indicates that these studies have no focus on the effect of LDPE on the adhesion between the bitumen and minerals. Hence, this study aims to model and evaluate the interfacial adhesion performance between the LDPE modified bitumen and different. MD simulations are employed to model the interfacial interaction between minerals and bitumen. Additionally, two representative minerals (quartz and calcite) have been selected to build the mineral-bitumen interface models. Results indicate that LDPE can improve the interfacial adhesion between the bitumen and minerals (quartz and calcite). Oxidative aging adversely affects the work of adhesion between the bitumen and quartz while positively affects the adhesive bond energy between bitumen and calcite. On completion of the MD simulations, it was found the different mixing process: dry method and wet method can affect the adhesion performance of asphalt binder. Moving onto the wet method, the work of adhesion between the bitumen and mineral increases once the LDPE directly mixes with bitumen. However, the work of adhesion between the bitumen and mineral decrease once the LDPE is introduced by dry method. This study provides a fundamental understanding to the combined effect of oxidative aging and LDPE on the adhesion between the bitumen and minerals at atomistic scale.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Dr Yuqing Zhang for providing me the opportunity to do this research. I appreciate the advice and direction he gave in regard to both my research and future career endeavors.

TABLE OF CONTENT

CHAPTER 1 INTRODUCTION

1.1 General Background

Road construction has played a vital role in the world owing to the impetus it provides to the economy. The UK has become the second largest road network in the EU which is 4.5 million km. To meet the supply and demand from the logistic, the sector of transportation keeps increasing dramatically with economic development. There are more requirements for road industry with high-quality road materials and pavement structures. Since 1921, most of the UK roads have been constructed by asphalt mixtures (David,1996) in P25. This is because the asphalt mixture has the advantages of smooth surfaces, low noise and easy to maintain. However, different types of pavement have different properties and serve different proposes depending on the traffic level, climate and other factors. In the UK, all roadways are designed to meet the following engineering performance including resistance to the cracking, deformation and durability over time. A better road design and construction can help to meet the demands for the aforementioned qualities, however, the combined the effects of the environmental factors such as solar radiation, moisture, temperature and the oxidative ageing may lead to the deterioration of flexible pavements which were built with the asphalt mixtures.

Since the revolutionary discovery of plastic, polymers have been experimented continually to meet a variety of applications. Plastic has become prevalent in our lives because the plastics are used for the conveniences of everyday life. As shown in the figure 1.1, it is reported that the plastic production was increased dramatically from 1.1million tones in 1950 to 362 million tones in 2015. Most countries especially in the UK, have disposed the plastics by land filling. However, the improper disposal of plastic such as low-density polyethylene (LDPE) could bring human health and environmental risks. This is because that the inappropriate use, disposal and recycling may lead to undesirable release of

potentially toxic substance. Based on the research, a current solution to minimize the risks from plastic is landfilling. Once plastics arrive at landfill sites, the landfills could take many years to degrade the plastic such as LDPE depending on the chemical property of the plastic.

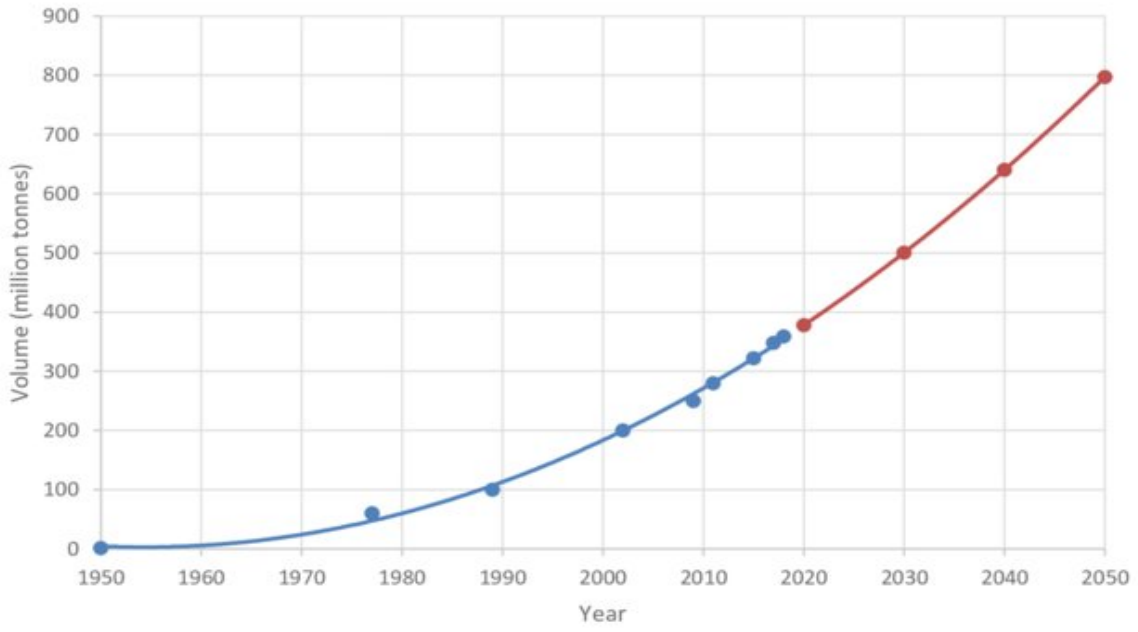


FIGURE 1.1 PLASTIC PRODUCTION FROM 1950 TO 2020 (READ AND WHITEOAK, 2020)

Previous research has highlighted that the incorporation of waste plastic or polymer into asphalt binder is an environmentally friendly approach for waste plastic disposal for road construction of flexible pavement and this method could be an efficient way to disposal the waste plastic as it is considered as a cleaner approach for sustainable future.

1.2 PROBLEM STATEMENT

Environmental factors could adversely affect the quality and properties of the asphalt binder. The primary reason is contributed by the adhesive failure (loss of adhesion between the asphalt binder and aggregate surface in asphalt mixtures). This is because, the asphalt binder (the bitumen) is known as a petroleum product which is a multicomponent material and composed of many types of components, ranging from the nonpolar to polar molecules. As a result, the interaction between different molecules

can determine the macroscale properties of the asphalt binder. The adhesion can be defined as the attraction force between the two molecules in the area of contract (Copeland,2007) in P57. Figure 1.2 shows the adhesion between the bitumen and aggregate. In the context of asphalt mixtures, adhesion may be used to refer to the amount of energy required to break the adhesive bond between bitumen and aggregate (Kanitpong &Bahia, 2003) in P8.

During the pavement construction and service life, the asphalt binder usually faces chemical changes that affect the chemical and mechanical properties of bitumen. This process is named as chemical aging. Previous study has reported that the oxidation of asphalt molecules could lead to hardening of asphalt and makes it more susceptible to cracking (Materin Martinez, 2015) in P108, Additionally, many studies also indicated that the mechanical and engineering properties of asphalt mixtures depend on the interfacial bond between bitumen and aggregate (Li and Greenfield, 2013) in P10. Therefore, the stronger adhesion can improve the engineering performance of the pavement.

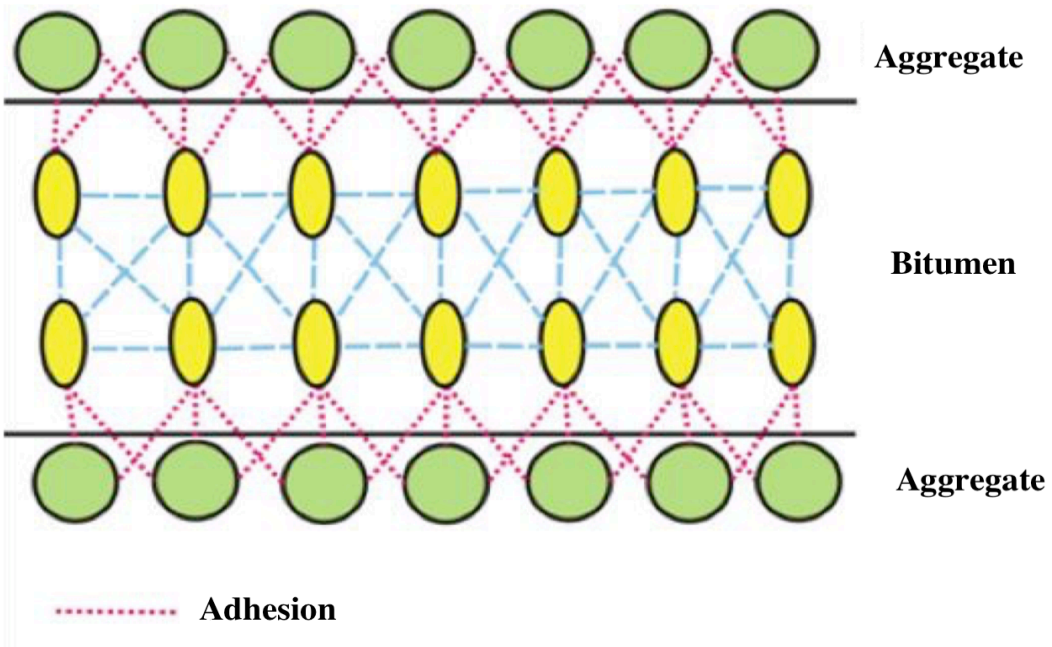


Figure 1.2 Adhesion present between bitumen and mineral. (Source: Adhesive.org 2010)

Most of the researcher found that the asphalt binders usually face rutting, fatigue cracking and moisture damage due to the weak interaction between the aggregate and bitumen. Some experimental studies have shown that the chemical aging significantly affect the stripping (moisture damage) properties of asphalt mixtures (Coree, 2005) in P27.

Various experiment test methods such as Fourier transform infrared spectroscopy have been used to understand the mechanism for interfacial adhesion between the bitumen and the aggregate surfaces(Copeland, 2007) in P2.With the development of the molecular and atomistic modelling, this method is one of the most effective method to analysis the material properties and system behaviors. For instance, a model system of the bitumen has been developed by Zhang and greenfield (2014). The molecular dynamic (MD) has been used to investigate the molecular interaction and the fundamental material properties of the bitumen (Claudy et al, 2015) in P4. Xu and Wang (2016) studied the adhesion between the bitumen and aggregate by using the MD method.

In recent years, many researchers found that the plastic is a cheap material for modification of bitumen as it can enhance pavement properties. For example, Nkanga et al. (2017) reported that the low-density polyethylene (LDPE) can be used for asphalt binder modification to improve the durability and fatigue resistance of asphalt. Similarly, Zoorab&Suparma (2000) indicated that the adhesion between the mineral and bitumen is improved by incorporating the LDPE into bitumen. Therefore, the LDPE is considered as one of the additives which can be used for asphalt binder modification to increase durability and fatigue life. However, most of research focus on the effect of oxidative aging and aggregate on the adhesion and there is no established study refers to the effect of LDPE on the adhesion between the bitumen and aggregate at the molecular scale, research in this area is crucial and evidently needed. The emphasis of this study is focused on the Molecular dynamic (MD) simulation which are

applied to build asphalt models with a different aging degree and further to evaluate the effect of LDPE and aging asphalt on asphalt performance of bitumen-aggregate interface in this research.

1.3 Research Aim & Objectives

This study aims to investigate the effects of LDPE and oxidative aging on the interfacial adhesion performance between different minerals and bitumen, when the LDPE is used in the asphalt mixtures using different (dry and wet) processing methods. This is because, the LDPE additive, both of processing method and bitumen aging as well as the mineral components can affect the chemical or mechanical properties of the LDPE modified asphalt binder at molecular scale and further affect the adhesion performance with mineral surfaces. In this thesis, the MD simulation investigation can help to understand how the changes in the molecular level of asphalt binder due to LDPE additive and oxidative aging can alter the adhesive performance of the bitumen-mineral interfaces.

To fulfill the main research aims of this research requires the following research tasks to be conducted, which correspond to individual objective:

- To understand the mechanisms of bitumen aging at atomistic scale
- To analyze the effect of asphalt oxidation on interfacial adhesion between bitumen and aggregate at the atomistic scale.
- To review the effect of different aggregate on the adhesion performance of bitumen-aggregate interface
- To understand whether and how the different mixing processes (dry and wet) for incorporating the LDPE into bitumen can affect the adhesion performance for aggregate-LDPE modified bitumen model.

- To compare different bitumen – mineral interfacial systems to investigate the combined effects of these factors (mineral types, ageing, processing methods) on adhesion property of bitumen-mineral interface.

1.4 Organization of Thesis

This dissertation presents, introduction, literature review, methodology, data analysis and conclusion. A brief description of each chapter is summarized as below.

Chapter 1: provides an introduction of the research. This section includes the social issues and environmental issues of plastic waste and the concept of LDPE incorporation in bitumen modification and road pavement application.

Chapter 2. describes a comprehensive literature review focusing on research aspects related to asphalt composition, molecular dynamic studies on asphalt and plastic (i.e. LDPE) modified bitumen. Finally, the research gap was identified. All of this led to the formation of research aims and objectives.

Chapter 3. presents the methodology used in the research. This dissertation will conduct the MD simulation to investigate adhesion performance for different mineral-bitumen models. A brief introduction to MD simulation and the theory of Molecular dynamic (MD) simulation are both provided in this chapter.

Chapter 4. provides the results obtained from this study. Data analysis is carried out to evaluate whether LDPE waste can improve the adhesive bond energy between the mineral and bitumen.

Chapter 5- draws firm conclusions of the research. The effects of LDPE and oxidative aging on the adhesion performance of asphalt binder is discussed, along with limitation and future experimental recommendations to enhance the performance of research

CHAPTER 2 LITERATURE REVIEW

In the first section, studies focusing on aspects related to the bitumen are reviewed and the literature review will carry out for the understanding and review of the research works done in the past 15 years on the bitumen modification by plastics (i.e. LDPE) for improvement of overall performance of asphalt mixture for road pavement and the mixing methods used for bitumen modification. In the section 2, adhesive failure that occur between the bitumen and mineral surface will be introduced, and the theory of adhesion of the bitumen-mineral interfaces is discussed as well. In the section 3, previous studies on asphalt binder and LDPE are reviewed, focusing on the studies related to asphalt composition, bitumen aging and molecular structure of LDPE. Finally, the last section presents the research gap derived from the literature review.

2.1 STUDIES ON BITUMEN AND USE OF WASTE LDPE IN BITUMEN

The bitumen is a highly viscous material which has good adhesive nature. With the economic growth and expanding population, recycling the plastic waste has been considered as a threat to human life. According to the report published in 2004, many virgin polymers such as LDPE have been used to incorporate in many road applications for examination and analysis to see whether bitumen can improve the engineering properties (Rahmen,2004) in P7.

2.1.1 Chemical compositions and ageing of bitumen

This section provides a review of the studies on asphalt binder, focusing on aspects related to bitumen composition and aging.

2.1.1.1 CHEMICAL COMPOSITIONS OF BITUMEN

The molecular structure of bitumen is highly depending on the chemical composition of bitumen. However, the chemical composition of bitumen varies based on the source of the crude oil from which the bitumen originates. Branthaver et al (1993) stated bitumen molecules are predominantly hydrocarbons (88%-90% by weight). The bitumen also contains the heteroatoms such as Nitrogen (0-1%), Oxygen (0-1.5%) and Sulfur (0-6%), and present along with trace quantities of minerals such as nickel (almost 200 part per million), vanadium (almost 2000 parts per million) , iron and magnesium, which are usually present in the form of inorganic salts and oxides.(Speight, 1999 in P8; Jiménez-Mateos et al,1996 in P8; Mortazavi and Moulthrop,1993 in P32; Read and Whiteoak,2003 in P8). Bitumen is believed to consist of close to a million different organic compounds, without a single pure compound dominating its property (Wiehe et al,1996) in P9. Therefore, bitumen has an extremely complex chemical composition, and this complexity leads to characterize the properties of bitumen such as chemical property and physical property difficultly. Therefore, Corbett (1969) summarized the systems of bitumen can be divided into two board based on the selective adsorption-desorption method (see Figure 2.1). According to their size and solubility in polar, non-polar or aromatic solvents, the chemical system in the bitumen can be further separated into four fractions chemically by its content of hydrocarbon compositions (Lu and wang ,2010) in P9. The four fractions of bitumen are named saturates (S), aromatics (A), resin (R) and Asphaltenes (A), which can also be called SARA. The main characteristics of these four different fractions are discussed as below.

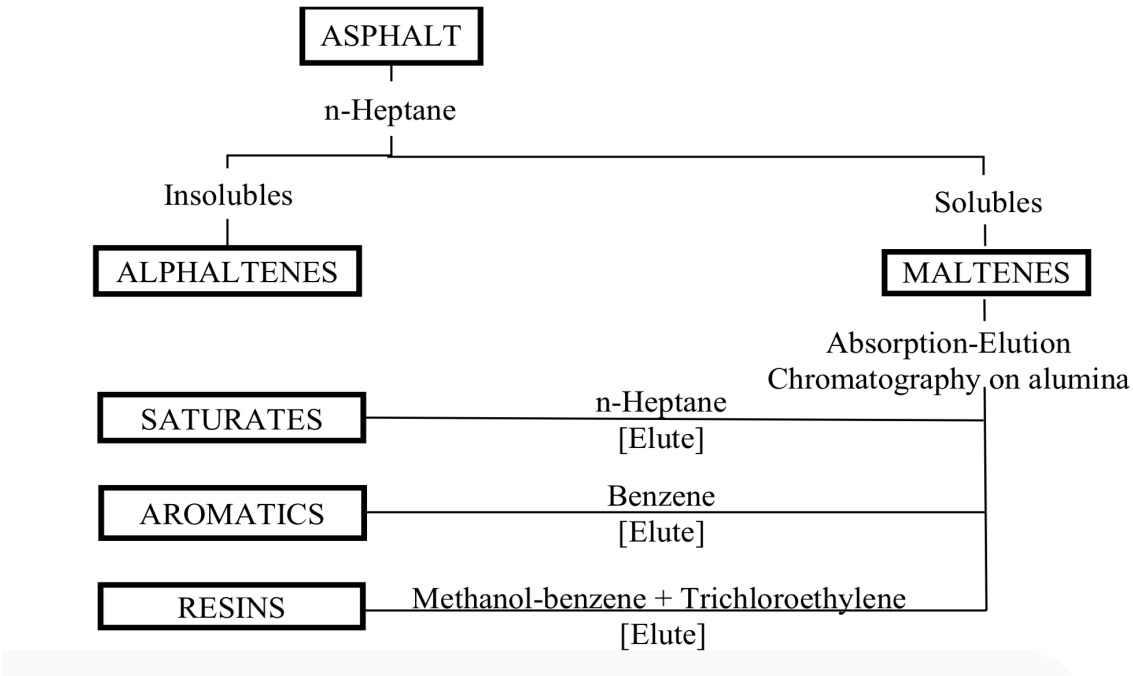


Figure 2.1. Schematic of Corbett's (1969) bitumen separation method based on bitumen fractions' size and solubility in polar and non-polar

- **Asphaltenes**

Asphaltenes are the largest and the most polar components of asphalt, making the largest contribution to its viscosity (Mullin,2010) in P25. Asphaltenes constitute 5 – 25% of the bitumen by weight and are defined as the fraction of asphalt that is insoluble in light alkanes of n-pentane, n-hexane or n-heptane, but is soluble in aromatic solvents such as benzene or toluene. Asphaltenes are mainly resulted the black color of the asphalt. This is because, the asphaltenes present an insoluble black amorphous solid at the room temperature, and do not exhibit thermal transition until the temperature up to 200°C (Lesueur,2009) in P91. Asphaltenes act as the viscosity—building agents and are also considered to be the most and largest polar aromatic materials (5-25%) in the bitumen and asphaltenes have a strongly effect on rheological and mechanical properties of bitumen (Mullins,2010) P7. As a

result, a review by Lesueur (2009) on the composition of asphaltenes noted that the asphaltenes are not only composed of aromatic components, it also includes a large number of heteroatoms such as oxygen, sulfur, nitrogen. This is because, the asphaltene comprises polar components and it has a very high tendency to interact and incorporate in heteroatoms (Lira-Galeana and Hammami, 2006) in P8. Therefore, they are considered to be aromatic compounds with alkyl chains and heteroatoms (Li and Greenfield,2013) in P107. In order to further understand the asphaltenes, many bitumen molecular models have been studied. The asphaltenes can be separated into island and archipelago types. Island models showed the asphaltenes include fused aromatic ring (FAR) with aliphatic chains. Archipelago supports the idea of asphaltene composed FAR with aliphatic short chains (Martin Martinez,2015) in P9.

- **Saturates**

Saturates constitute 5-15% by weight of bitumen and show glass transaction in the temperature about -70°C (Corbett,1969) in P6. Saturates are light and non-polar molecules which consist of aliphatic chains (n-paraffins) with branched (iso-paraffins) and cyclic alkanes (Roberts et al,1996) in P55. The saturate fractions show the low chemical reactivity and rarely changes with times as they are highly resistant to ambient air oxidation (Petersen, 2009) in P7. At room temperature, Saturates present colourless or straw liquid.

- **Aromatics**

Together with resins, aromatics and resins are the most abundant component in asphalt, constituting 30-45% of the total bitumen. Aromatics consists of non- aromatic rings and non-polar

carbon chains (Corbett,1969) in P6. The aromatic is the softening element in the bitumen. It has good dissolving ability for paraffin waxes and It also has a light molecular weight hydrocarbon and present a yellow to red liquid at room temperature. it is more viscous than saturate due to higher glass traction at same temperature. Claudy et al (1992) stated the aromatic can easily react to the oxygen atoms during 18-year service period. Aromatics are more viscous than saturates at the same temperature, but less viscous than resins (Claudy et al 1992) in P6.

- **Resins**

Resins, are also considered to be polar aromatics, consists of nonpolar paraffinic groups and heteroatoms containing oxygen, sulfur and nitrogen. Therefore, they are also gaining fraction in the bitumen (Lira-Galeana and Hammami, 2007) in P8. At the room temperature, Resins are black solid in bitumen as it cannot exhibit a glass traction.

2.1.1.2 Oxidative Aging of Bitumen

The chemical aging of bitumen can result in hardening and brittleness in bitumen, causing the cracking in pavement. Bell (1989) studied aging occurring at two stages, which are short-term aging and long-term aging, respectively.

The short-term aging happens during the mixing of asphalt binder. This is because, the bitumen is heated up to 160°C in order to reach sufficient workability for mixing and construction. Once the temperature is increased to 160°C, the low molecular weight fraction of bitumen is evaporated, resulting in an increase in of asphalt binder. Normally, this stage can be simulated by Rolling Thin Film Oven (RTFO) in the laboratories.

The long-term aging occurs over the 10-15 service life of asphalt mixture. Different to the simulated method of short-term aging in the laboratories, the long-term stage aging usually simulated using the pressure Aging Vessel (PAV) method (Boysen et al, 2015 in P9 and Qin, 2014 in P17). Peterson (2015) reported the change in SARA factions of bitumen can be used to characterise the aging of bitumen. According to the study from Peterson (2015), during the aging process, resins and asphaltenes in the bitumen are both increased in bitumen and there is a decrease in aromatic content (Corbett, 2014) in P10. This is because the aromatics in the bitumen is converted into the resins, and then the resins are converted into the asphaltenes (NCAT, 2014) in P1. In terms of stature fractions, many studied reported that there is no change occurs because the stature has a low reactivity (Perterson ,1993 in P90; Khabaz ,2015 in P10 and Daly et al ,2010 in P29).

- **Oxidative aging of functional groups in bitumen**

Based on the study by Petersen (1984), he stated when the bitumen is exposed to atmospheric oxygen in the road or pavement, the bitumen rapidly oxidizes and forms polar function groups which can alter rheological properties of asphalt mixture .The investigation of oxidative aging bitumen can be narrowed down to the certain types of functionalities, as there are many bitumen molecules share these chemical functional groups. (Pertersen 1986). Peterson and Glaser (2011) investigated ketone and sulfoxide chemical functional groups can be identified as two major chemical functionalities after oxidative aging (see Figure 2.2). As shown in the Figure 2.2 (a), the ketones are formed once the oxygen attached to benzylic and the carbon atom is replaced by the oxygen atom. The sulfoxides are a chemical functional group containing a sulfinyl functional group, S=O, attached to two carbon atoms. Sulfoxides formed at sulfur atoms in bitumen when the oxygen is introduced into the sulphide function. (see Figure 2.8 b)

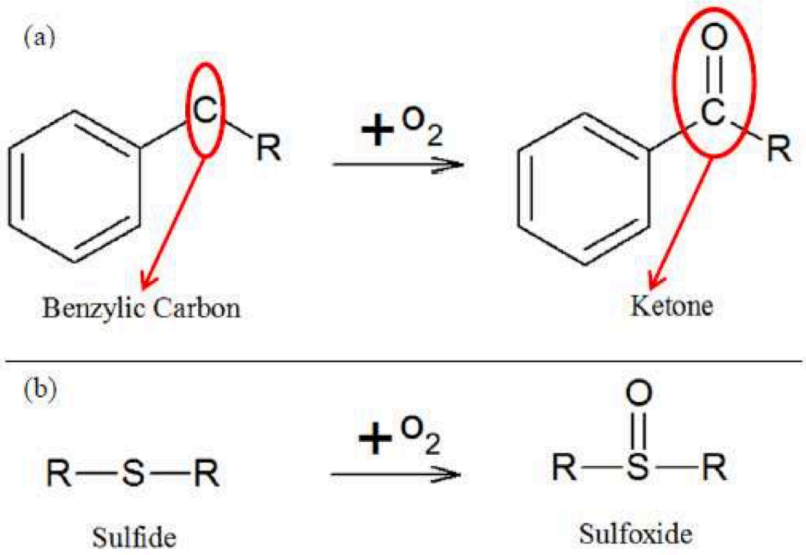


Figure 2.2 Formation of ketone and sulfoxide, from Pan and Tarefder (2016)

2.1.2 Plastic waste as an asphalt binder additive.

The use of polymer for asphalt binder modification in paving roads has been started since 1990s. The polymers are well-known additives for improvement of mechanical properties in asphalt binders and the main advantage of plastic modified bitumen is higher fatigue life in that it has a good adhesion performance between bitumen and aggregate. Therefore, many experts start using the virgin polymer in bitumen as an additive.). An alternative approach is to use the 'recycled polymer' or 'waste plastics' rather than the virgin form to reduce the cost of the polymer. This has led to many efforts undergone to distinguish the different types of plastics. There are 7 divisions of recycled plastics (see Figure 2.3). However, different types of the plastic can enhance the engineering properties of modified bitumen differently. The table 1 outlines advantages and disadvantages as implication of different plastic asphalt binder in road construction.

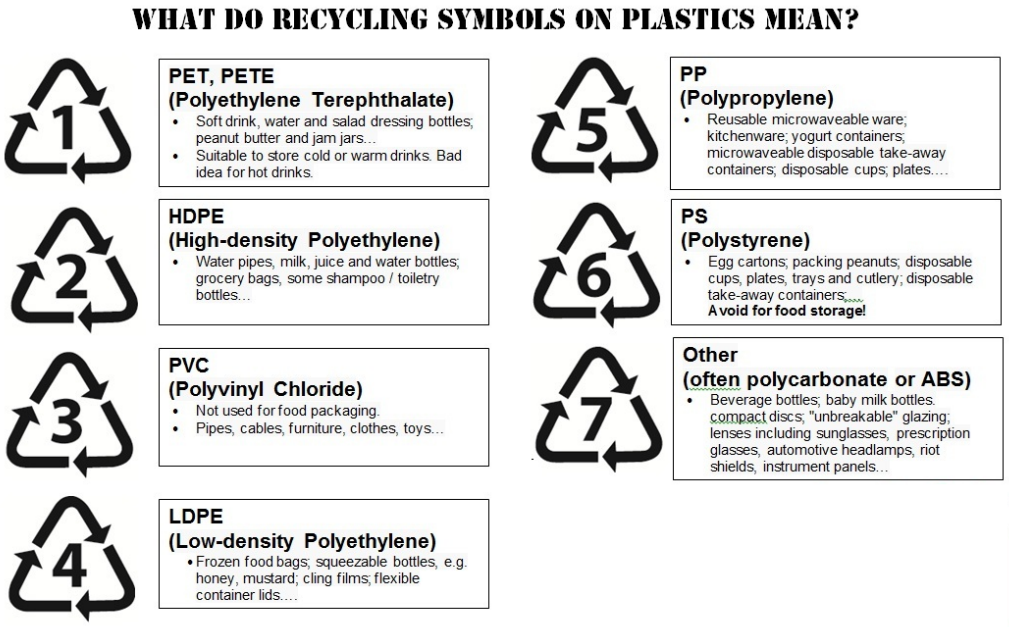


Figure 2.3 Seven divisions of waste plastic (IKA, 2019)

Table 1: Advantages and disadvantage of different plastic asphalt binder in road construction

(Source: Sen and Raut,2015; Hindle,2019, AZO materials,2012 and Rahman 2004).

Different types of waste plastic	Melting point (℃)	Dynamic modules	Viscosity increase	Low temperature cracking (BBR test)	Phase angle reduction	Conclusion
Polyethylene (PE)	110-120(LDPE) 130-150 (HDPE) 125-170 (PET)	Increase	270% (125 ℃)	Improve	Decrease	- Higher modules - High temperature resistance implies a greater rutting resistance - Ageing performance is greater than conventional binder - Increased the viscosity
Polypropylene (PP)	135-160	Remain constant	63-410% (135℃)	Improve	Decrease	- Increased the viscosity. - Higher resistance to permanent deformation. - Low thermal fatigue cracking resistance.
PVC	Around 300	Increase	Up to300% (135 ℃)	Improve	Decrease	- Low cracking and better fatigue resistance - Increased the viscosity

As can be seen from the Table 1, the LDPE shows better performance in improving the engineering performance such as the resistance to rutting and ageing in comparison to the other types of waste plastic. Thus, the LDPE is selected as the research subject in this study.

2.1.3 LDPE modified bitumen

The waste plastic such as LDPE, PET and HDPE, has been found to be a good modifier of bitumen. In 1981, the PE was the first plastic introduced into the bitumen as binder. Denning and Carswell (1981) decided to use NOVOPHLAT (which is made of PE) at 7% by weight of bitumen mixture into the asphalt binder. The result reported that asphalt mixture using polyethylene modified binder were more resistant to permanent deformation at high temperature (Deneing and Carswell, 1981). Therefore, Reinke and Gidden (2002) studied the engineering properties of LDPE modified bitumen and founded that 5% LDPE concertation by weight can enhance the physical properties of bitumen. They founded that the penetration decreases as compared with the unmodified bitumen while the softening point and viscosity increase. Another study of notable findings suggested utilizing LDPE modified bitumen is a better binder compared to bitumen without additive resulting higher Rutting resistance and better fatigue performance (Uddin et al,2004) in P19. Vasudevan (2007) claimed that the LDPE modified bitumen has a better rheological property and keeping the values of ductility at minimum range of specification comparing to the performance of neat bitumen.

Ahamdainia, et al (2010) showed that waste LDPE in various percentages such as 0%, 2%,4%, 6% and 8% could blend with bitumen mixture The result showed the incorporation waste LDPE into the bitumen can improve the resistance against permanent deformation (rutting) and increase the stiffness of the asphalt binder as compared to the conventional bitumen mixture. Vargas et al (2013) summarised the advantages of LDPE modified bitumen are lower temperature susceptibility, better age resistance

properties, higher fatigue life and higher resistance properties, higher resistance to deformation at higher temperature. With that the LDPE modified bitumen has a better adhesion property between aggregate and binder, which meliorates the performance properties in heavy traffic and extreme climatic conditions. Babalghaith et al (2018) carried out an experiment to study rheological properties of Polyethylene modified bitumen. The study used LDPE, high density polyethylene (HDPE) and Polyethylene terephthalate (PET) to modified virgin bitumen. they found the rheological properties of Polyethylene modified bitumen is very sensitive and depends on external factors such as the mixing duration and mixing methods, and internal factors such as type of bitumen and type of polyethylene. The study also reported that LDPE modified bitumen offers a better rheological performance in comparison with PET modified bitumen and HDPE modified bitumen.

2.1.4 Blending plastics in bitumen

The recycled plastic has been incorporated into asphalt mixtures by two distinct processes known as "dry process" and "wet process" (see Figure 2.4). A short definition for each process is presented below:

- **Dry Process**

In this technology, the polymer is directly added to the either aggregate or bitumen. Therefore, this method is suitable for blending the polymer with aggregate and bitumen without using any special equipment. However, the degree of interaction between the binder and polymer could be affected by grading, size of polymer, mixing time and mixing temperature (Brule,1995) in P17. Therefore, this technology can only be used to blend coarse polymer with less specific surface area. This could result in very slight interaction and has no significant effect on the properties of the bitumen as compare to the wet process.

- **Wet Process**

Wet method is the most common method of manufacturing the polymer modified bitumen. According to McDonald's technique, the polymer must be added to the bitumen before mixing with aggregates. They are mixed at high temperatures for a given times to promote the physical and chemical interaction and to achieve a homogeneity. Therefore, if a study is only looking at polymer incorporation into the bitumen binder before production of asphalt cement, only the wet method can be considered. However, most of published studies prefer to use the wet method to produce the polymer modified bitumen as it can make a large amount of the modified binder (Brasileiro et al,2019) in P11. Blending the polymer in bitumen can increase the viscosity of binder and it could bring construction challenges due to the high viscosity.

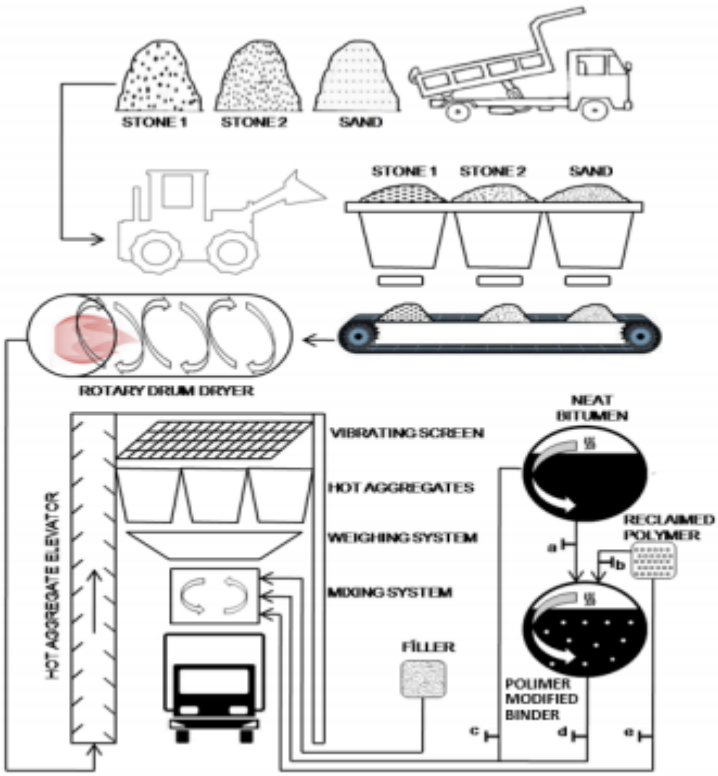


Figure 2.4. Wet and dry processes for polymer incorporation into bitumen. (Brasileiro et al. 2019)

2.2 Adhesive and Cohesive in Bituminous Materials

In this section, Firstly, the adhesion theory and cohesive theory are both presented. The definition of adhesion and cohesive energy between the bitumen and aggregate as well as the cohesive energy are also presented. The influences of chemical composition and types of aggregates on the adhesive strength between bitumen and aggregate are discussed as well.

2.2.1 Theory of Adhesion

Hicks (1991) has investigated that there are four board theories which has been used to explain the theory of adhesive bond energy between the bitumen and aggregates, namely as molecular orientation theory, chemical reaction theory, mechanical adhesion theory and surface energy theory.

- **Molecular orientation theory**

Rice (1959) has found the adhesion is established when the bitumen and aggregates are bought in contact. Therefore, the theory of molecular orientation claims that molecule of bitumen tends to orient itself in order to satisfy the energy demand of the mineral surface when the bitumen is contact with the mineral. Moreover, Bhasin et al (2006) stated that molecules of bitumen are non-polar (Lifshitz-van der Waals) generally, although some component are polar (Lewis acid and Lewis base).

- **Chemical Reaction Theory**

Terrel and Shuttle (2012) described the chemical reaction theory has been accepted to explain the effect of types of aggregate on the interfacial adhesion between the bitumen and aggregate. According to the findings from Teerel and Shuttle (2012) as shown in Figure2.5, aggregates can be classified into either hydriohilic (acidic mineral) or hydrophobic (alkali mineral). The major chemical properties of

the minerals that determine the characteristics of either hydrophilic or hydrophobic are surface chemistry, porosity and pore size.

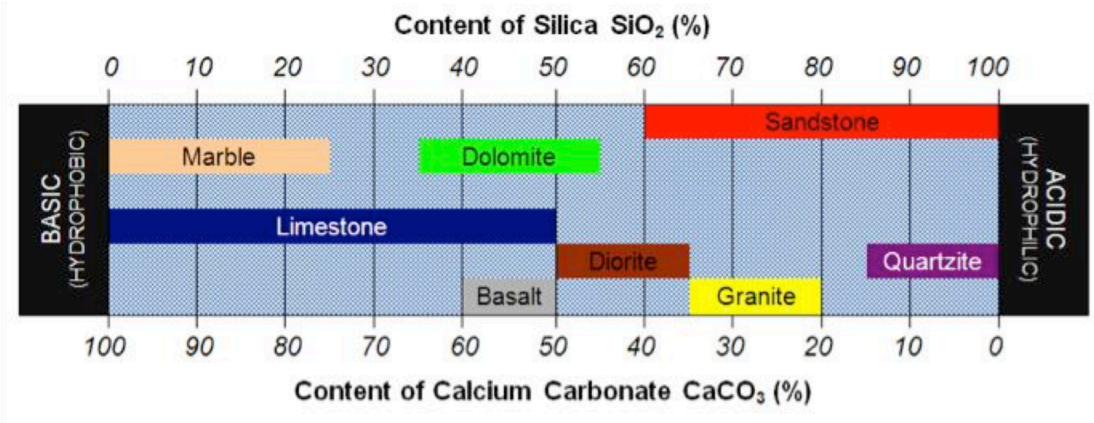


Figure 2.5 Classification of aggregates as hydrophilic and hydrophobic (Source: Huang 2004)

Huang (2004) summarized the acidic minerals such as quartzite is less likely to form bonds as strongly with the bitumen. The pH values of the surface of an aggregate can affect adhesive bond energy of the asphalt binders. In other words, a more acidic aggregate surface is hardly to form strong bond energy between the bitumen and surface aggregate (Graf, 2010) in P27. The increment of the pH value of asphalt binder is not restricted to the acidic mineral, but also occurs with the alkali mineral. Hence, the classification of the aggregates as either acidic aggregate or alkali aggregate can only be used as rough assessment rather than absolute.

Hick (1991) indicated the PH value of bitumen also can affect the adhesion between bitumen and aggregates. Many past studies have found the pH value of the bitumen could be increased once oxygen atoms are introduced into the asphalt binder (Huang et al, 2000 in P10; Labib,1992 in P17; Scott ,1978

inP205; Yoon & Tarrer,1988 in P109). Therefore, the pH value of bitumen surface could be increased with the increased content of oxygen in the bitumen (Yoon & Tarrer, 2000) in P10.

- **Mechanical adhesion theory**

Terrel and Al-Swailmi (1994) investigated the machinal adhesion theory has been accepted to explain the effect of physical properties of aggregate such as particle size, contacting surface texture absorption and porosity on the adhesion between the bitumen and aggregates. A stronger adhesive bond energy between bitumen and aggregate can be created when bitumen gets into the surface irregularities and pores of the aggregates, causing a mechanical interlock. However, according to Tarrar and Wagh (1992), aggregate having smooth surface texture are harder to create mechanical interlock as compare to the rough surface.

- **Surface Energy Theory**

Hick (1951) defined the surface energy theory is defined as the adhesive bond energy needed to create a unit area of contact between aggregate and bitumen in vacuum condition. According to the Rice (2008), in order to create an effective adhesive bond energy between the bitumen and aggregate, the bitumen must be completely coated the surface of aggregate. The coating ability of bitumen can be defined as surface energy theory (Kringos et al,2010). Therefore, the adhesion tension can be established when the bitumen and a surface of aggregates are bought in contacted. Some past studies found the adhesion between the aggregate and bitumen can be varied with the types of aggregate, physical properties of aggregates and the chemical composition of bitumen (Bhasin et al. 2006; Cheng et al. 2002).

2.2.2 Cohesive energy theory

In the context of asphalt mixture, the cohesion refers to the intermolecular force within the bitumen. The cohesion strength is affected by the rheology of bitumen in the asphalt mixture. Therefore, Kim (2013) described in more detailed subsequently, the cohesive energy is mainly used to resist the microcrack in the asphalt binder, which is strongly affected by the dispersion of aggregate. Therefore, the cohesive energy in the asphalt binder is not only controlled by the bitumen alone, but by the combination of bitumen and aggregate. Teeral (1994) indicated that there are several factors such as temperature, moisture content can affect the cohesion in the bitumen. Based on the Cheng (2005), the moisture can affect cohesive bond energy including weakening the bitumen as moisture saturation expansion so it can cause asphalt binder to lose stiffness and durability.

2.2.3 Adhesive failures

Adhesion failure normally happens at the interface between the adhesive layer and substrate (Yonn&Tarrer,1988). As has been stated before, adhesion is a molecular force of attraction in the area of contact between adhesive and substrate which can act to hold the bodies together (Copeland,2007) in P19. Therefore, in the context of asphalt binder, the adhesion usually refers to amount of adhesive bond energy required to break the adhesive bond between bitumen and aggregates (Kanitpong&Bahia,2003) in P10. Some studies stated that the adhesion failure refers to the displacement of aggregates from the bitumen surface, which indicates low magnitude of adhesive bond strength (Shatanawi et al ,2012 in P10; Martin,2015 in P37). As shown in the Figure 2.6, the adhesion plays vital role in the asphalt mixtures.

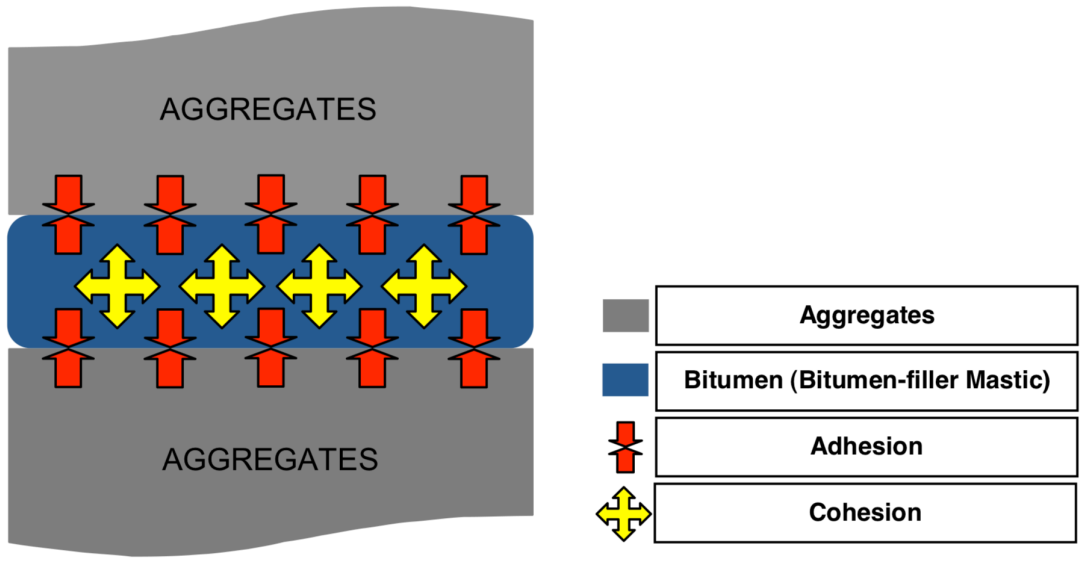


Figure 2.6 Adhesion and cohesion of bitumen (bitumen-filler mastic) and aggregates (Source: Lytton et al. 2005)

Lytton et al (2001) stated that adhesive failure is mainly affected by the physical and chemical properties of asphalt binder. Based on the study conducted by Lytton et al (2001), Reed (2002) suggested that the adhesion tension between the bitumen and mineral varies with the types of aggregates and chemical composition of bitumen. In order to further analysis the adhesive failure, Little and Jones (2003) has tried to quantify the adhesion of various combinations of asphalt binder materials (i.e. bitumen and aggregates) by performing wheel tracking test. Based on the study, they concluded that the adhesive failure is mainly influenced by the properties of the aggregate rather than the properties of bitumen. Also, for hydrophobic (alkali) aggregates, the effect of different types of bitumen is almost negligible. This part of the study has correlated the adhesive bond energy of aggregates and bitumen with types of aggregate and chemical composition of bitumen. Using the experimental data from Little and Jones (2003), Curtel et al (2004) investigated the relationship between these parameters (types of aggregate, adhesive bond energy, chemical composition of bitumen).

- **Effect of chemical composition of bitumen on adhesion**

Bitumen acts as viscoelastic binder which is used to hold together aggregates or minerals particles in the asphalt binder. Bitumen is a complex hydrocarbon “liquid” whose chemical composition relies on the source of oil which is the bitumen originates (Wignall et al, 1991) in P18. Curties et al (1993) found there are two main chemical functional groups within the bitumen, which are maltene and asphaltene, respectively. The both groups have a significant effect on the property of rheology of bitumen (Reed,2003) in P29. According to the findings from Reed (2003) and Curties et al (1993), Whiteoak (2003) concluded that the different specific functional groups within the bitumen can affect the interfacial adhesion between aggregates and bitumen in terms of adsorption isotherm behavior at different levels (see Table2). As shown in the Table 2, the majority of function groups within the bitumen have shown the good adsorption behavior. This is because, the polarity and the separation charge within the bitumen molecule can promote the adhesive bond energy between the bitumen and aggregates (Little and Jones,2003) in P41. As can be seen from the Table 2 as below, the level of absorption depends on the absorbed functional group within the bitumen. For instant, the Carboxylic acids or anhydrides functional group in the bitumen could leads the bitumen strongly attracts to the aggregate surface but the ketones could make the bitumen tends to easily deboned under scrubbing action so that it can be also removed from the surface of aggregates easily (Curties et al,1993) in P76. Due to all chemical functional groups present or form in bitumen, the interfacial adhesion between the aggregate and bitumen becomes relatively stationary when the bitumen is coated with the aggregate (Robertson et al, 2001) in P9. However, the environmental factor such as high temperature can cause the “polarity alone” in the bitumen so that adhesion in the asphalt mixture cannot achieve a good level

because the polarity in the bitumen may not be sufficient. (Hicks,2001) in P72. As a result, the low level of absorption for the bitumen could cause the adhesion failure.

Table 2: Absorbed functional groups within the bitumen for aggregated surfaces. (Source: Caro et al,2008).

Absorbed functional groups (Increasing order)			
Level of Absorption	Curties et al. (1993)	Petersen et al. (1992)	Plancher et al. (1997)
Low	Kentones	Pyrridine	Kentones
		Pyrrolic	
High	Sulfoxides	Anhydrides	anhydrides
	Pyrridine	pyrrolic	sulfoxides
	Pyrrolic	pyrridine	pyrridine
	Carboxylic acids	Carboxylic acids	Carboxylic acids

- **Effect of types of aggregate on the adhesion**

Kandhal et al (1997) stated asphalt binder includes 92%- 96% aggregate by weight of asphalt binder, while the bitumen only accounts for about 4% and 8% only. Therefore, the aggregate is the most important part in the asphalt binder. The physical and chemical properties of aggregate play equally important role in determining how well the adhesive bond energy between the surface of aggregates and the bitumen so the properties of aggregate can directly affect the performance of asphalt binders. The physical properties of aggregate commonly are measured by the ability of resistance to crushing, stripping and particle shape (Cordon1979). Therefore, Miller& Bellinger (2003) investigated physical properties of aggregate can vary with the types of aggregate. For example, hydrophilic aggregates (e.g.

Granite and Quartzite) has a reactively low adhesive bond strength with bitumen as compare to the other types of aggregates. Therefore, hydrophilic (acidic) aggregates are easier to cause the adhesion failure. According to the chemical bonding theory (Hicks, 1991), the Bagampadde et al. (2005) and Caro et al (2008) noted the aggregate with high content of alkali feldspars (e.g. albite) cannot easily to strip as it has a strong adhesive bond energy to attract the bitumen. Bagampadde et al. (2006) found the alkali aggregate has a better ability of resistance to stripping and moisture damage than the acidic aggregate because the chemical bond of the acidic aggregate is not sufficient to attract bitumen (see Table3). However, Kim&Coree (2005) stated chemical properties of aggregate are very difficult to predict as chemical fraction of bitumen can be changed over period time during the aging process.

Table 3 Summary of aggregates according to the physical and chemical properties associated with them (Source: Cordon,1979 and Hick,1991)

Types of Aggregates	Resistance to crushing	Resistance to stripping	Particle shape
Grainte	Fair	Fair	Fair
Basalt	Good	Fair	Fair
Albite (Feldsaprs)	Fair	Poor	Good
Quartz	Fair	Fair	Good
Calcite	Good	Good	Fair
Chert	Good	Fair	Poor
Schist	Fair	Fair	Fair

2.2.4 COHESIVE FAILURES

Fromm (1994) investigated that the cohesive is the intramolecular force developed within the bitumen which can hold the molecules of bitumen and is influence by viscosity of bitumen. In the context of asphalt binder, the cohesive failure refers to the separation of molecules within the bitumen (John,2003) in P78. The cohesion failure generally reduces the cohesive strength within the bitumen

via softening and causing the bitumen to lose stiffness (Rand,2002) in P10. Therefore, the cohesive failure results in the reduced durability of asphalt mixture and increased permanent deformation. Si et al (2002) investigated the rheological properties of bitumen and dispersion within the bitumen are determined by the cohesive bond strength within the bitumen. The Canestrari et al (2010) conducted an experiment test and found the cohesive bond strength can be decreased at the temperature lower than 25 °C so that the moisture on the aggregate surface can be dispersed and reaches to the bitumen. As a result, the results indicated that the moisture can accelerate the cohesive failure within bitumen because the interaction with water molecules.

2.2.5 COMBINED ADHESION AND COHESION FAILURES

Rand (2012) stated the failure which happened within the asphalt binder is neither entirely adhesive nor cohesive. Therefore, Rand (2012) conducted an experiment study to identity the forms of failure as either adhesion failure or cohesion failure via visual observation. According to the study, Rand (2013) summarized the adhesion failure is more common than the cohesion failure in the asphalt binder. Rand (2013) also noted that there are three main types of failure which might possibly occur between bitumen and aggregates and he also stated the failure of for asphalt mixtures is usually neither entirely cohesive nor adhesive (see Figure 2.7). He concluded that the failures for asphalt mixtures are mainly affected by the properties of aggregate instead of properties of bitumen. Therefore, the adhesion failure is the main factor affects the performance of the asphalt mixture.

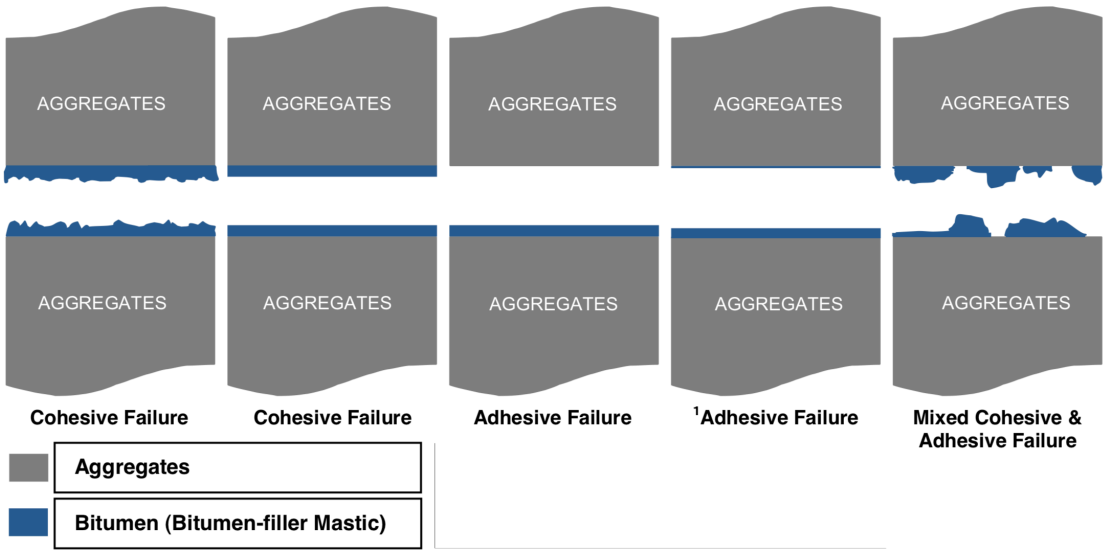


Figure 2.7. Possible types of failure that might occur in asphalt mixtures (source: Rand 2012).

2.3 MD Simulation of Bitumen and LDPE

2.3.1 The molecular dynamic simulation

To do molecular dynamic simulation of a complex and multicomponent material such as bitumen, the molecules of model can be used to represent the huge number of different elements within the bitumen.

Groenzin and Mullins (2010) proposed there are two asphaltene molecules were selected in the MD simulation, the one with the aromatic core and with a small branch, and one with aromatic core with long chain alkane side branch See Figure 2.8). Based on the study of Zhang and Greenfield (2007), Li and Greenfield (2014) proposed a 12-component model bitumen system to represent AAA-1, AAK-1, and AAM-1 bitumen of the Strategic Highway Research Program (SHRP). They founded the alkanes(n-paraffin) consists of long branches and cyclic alkanes but the content of alkanes in the saturate fractions is very low. As a result, they used the squalene and hopane to represent the saturate fractions in the bitumen.

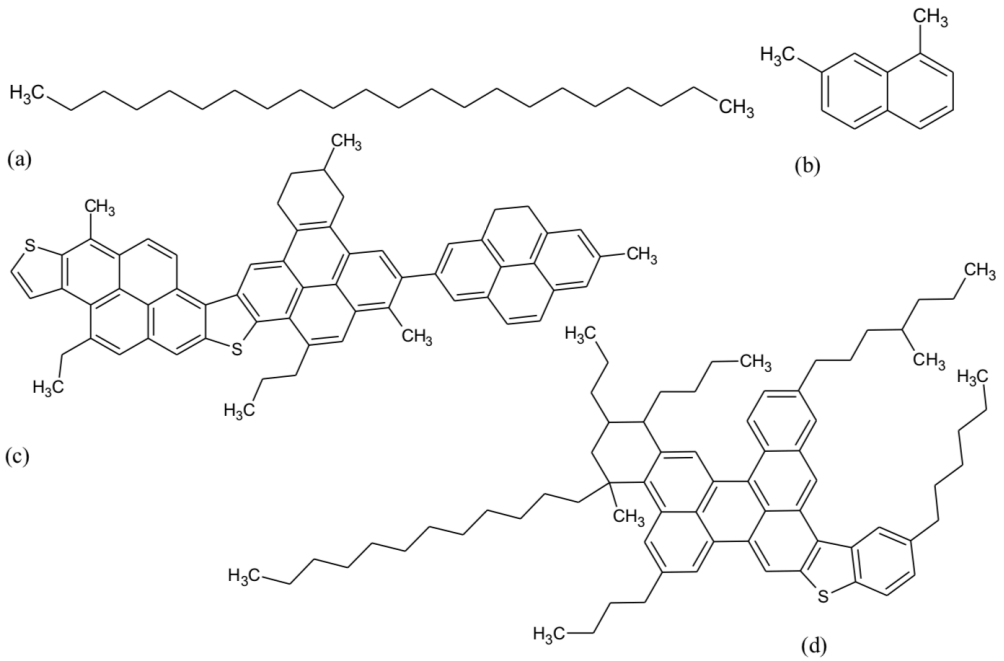


Figure 2.8 Molecules used by Zhang and Greenfield (2007) (a) n-docosane (n-$C_{22}H_{46}$), (b) 1,7-dimethylnaphthalene, (c) asphaltene 1, and (d) asphaltene 2

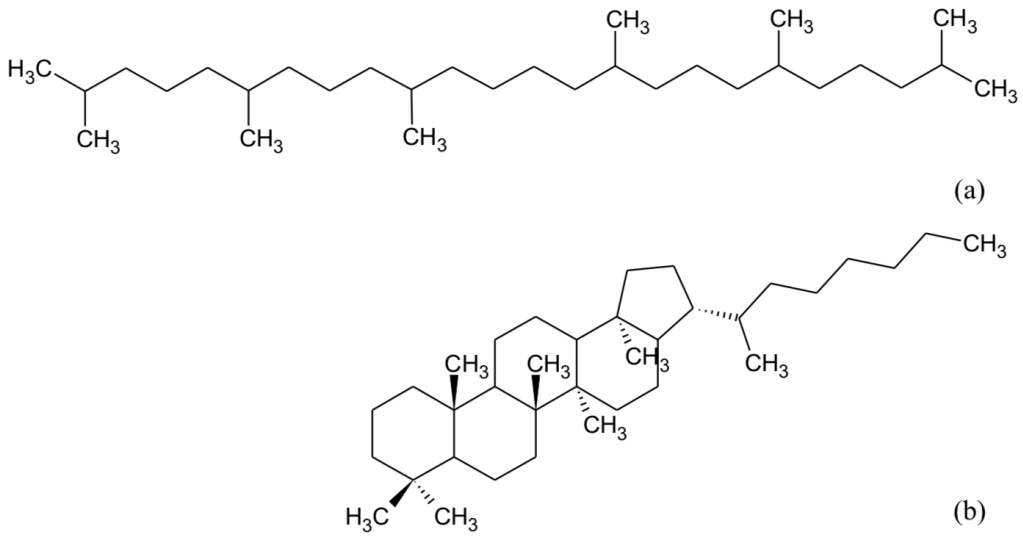


Figure 2.9 structures of saturates: (a) squalane and (b) hopane (Li and Greenfield 2014)

As can be seen from below, Figure 2.10 (a) and Figure 2.10 (b) show the two structures of aromatics fractions in bitumen, two molecules, namely dicotyl-cyclohexane-naphthalene (DOCHN) and Perhydrophenanthrene-naphthalene (PHPN), are selected to represent the two aromatics molecules in the bitumen (Li and Greenfiled ,2014). The PHPN is proposed by Simanzhekov (2003) and DOCHN structure is shown by Lira-Galeana (2000).

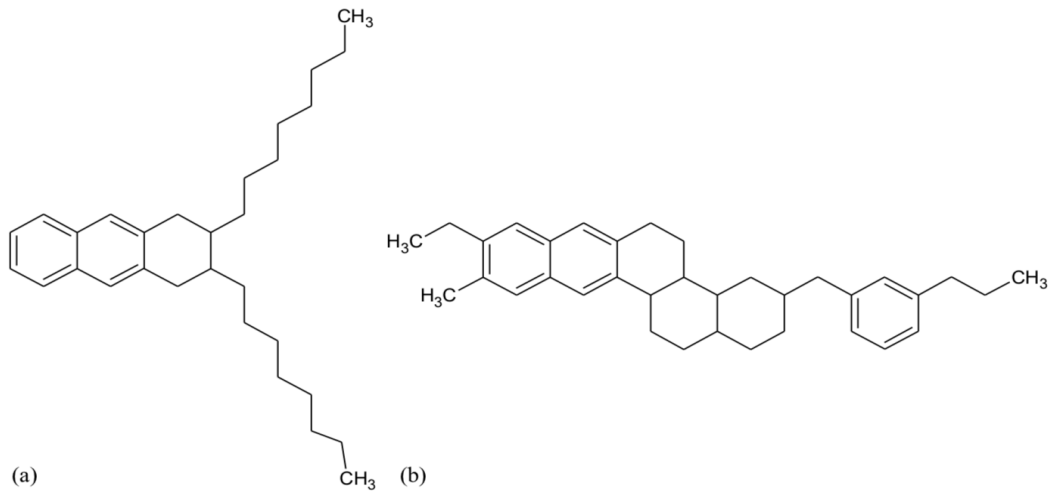


Figure 2.10 Structures of aromatics: (a) DOCHN and (b) PHPN (Li and Greenfield 2014)

Figure 2.11 shows five different molecules which are selected to represent the resin fraction in the bitumen. These five molecules are named as benzobisbenzothiophene, pyridinohopane, quinolinohopane, trimethylbenzene-oxane, and thio-isorenieratane, respectively (Li and Greenfield ,2014) in P10 In the context of bitumen, these molecular structures are proposed primarily from geochemistry literatures according to the analyses of petroleum found in sedimentary rock deposits (Li and Greenfield , 2014) in P11.

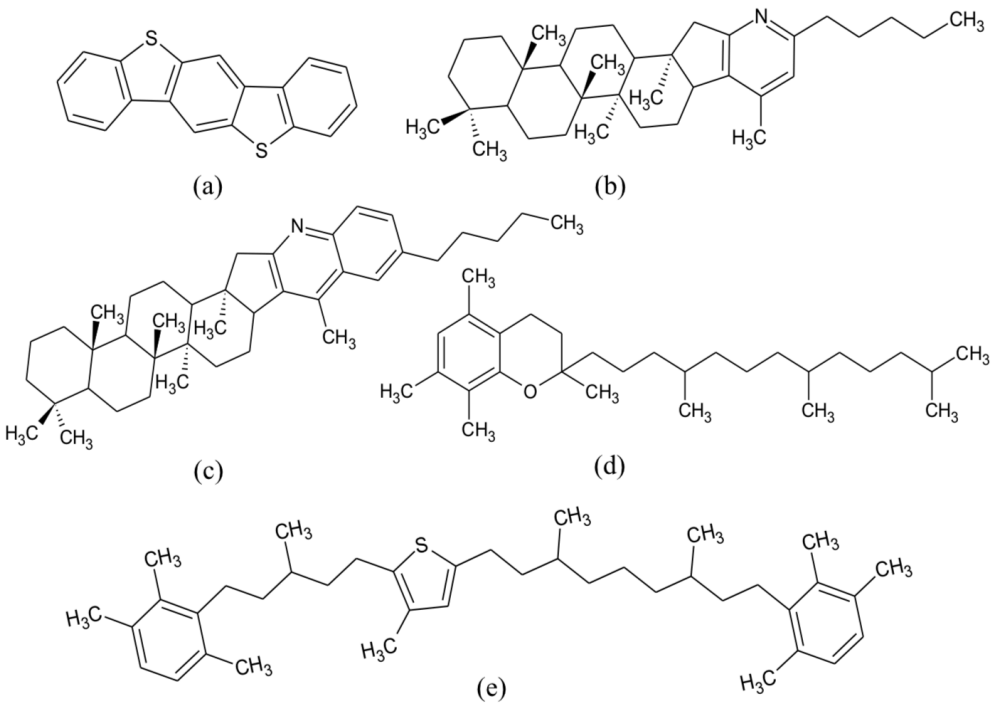


Figure 2.11 Resin: (a) benzobisbenzothiophene, (b) pyridinohopane, (c) quinolinohopane, (d) trimethylbenzene-oxane, and (e) thio-isorenieratane (Li and Greenfield 2014)

Martin-Martinez et al (2015) proposed modification to the asphaltenes used by Zhang and Greenfield (2007) and Li and GreenField (2014) which is more reflective of accurate structures of asphaltenes (see Figure 2.12). In In 1972 Erich Clar formulated his aromatic π-sextet rule that allows discussing qualitatively the aromatic character of benzenoid species. Now, 40 years later, Clar's aromatic π-sextet rule is still a source of inspiration for many chemists. This simple rule has been validated both experimentally and theoretically. In this review, we select some particular examples to highlight the achievement of Clar's aromatic π-sextet rule in many situations and we discuss two recent successful cases of its application. In 1931, Hückel formulated his renowned 4n + 2 rule that explain the stability of benzene as compared to cyclooctatetraene or cyclobutadiene. Since this rule is strictly valid only for monocyclic conjugated systems, several attempts were made to extend this rule to polycyclic systems.

Among them, the probably most successful was Clar's π-sextet rule formulated in 1972 in the book "*The Aromatic Sextet*" (Clar, 1972) in p27. This model was inspired by the work of Armit and Robinson who were the first to use the term aromatic π-sextet. Clar's rule states that the Kekulé resonance structure with the largest number of disjoint aromatic π-sextets, i.e., benzene-like moieties, is the most important for characterization of properties of polycyclic aromatic hydrocarbons (PAHs). Aromatic π-sextets are defined as six π-electrons localized in a single benzene-like ring separated from adjacent rings by formal CC single bonds. Based on the Clar sextet theory and density functional theory, they used three molecules, which are asphaltene-phenol, asphaltene-pyrrole, and asphaltene- thiophene, respectively to represent the asphalt fraction after modification (Li and Greenfield,2016) in P9. Comparison with previous models of asphaltene (see Figure 2.9). The distribution of p electrons in aromatic core is optimized and geomatical stain is also minimized within the three new molecules of asphaltene. The resulting asphaltene molecules are shown in the Figure 2.12.

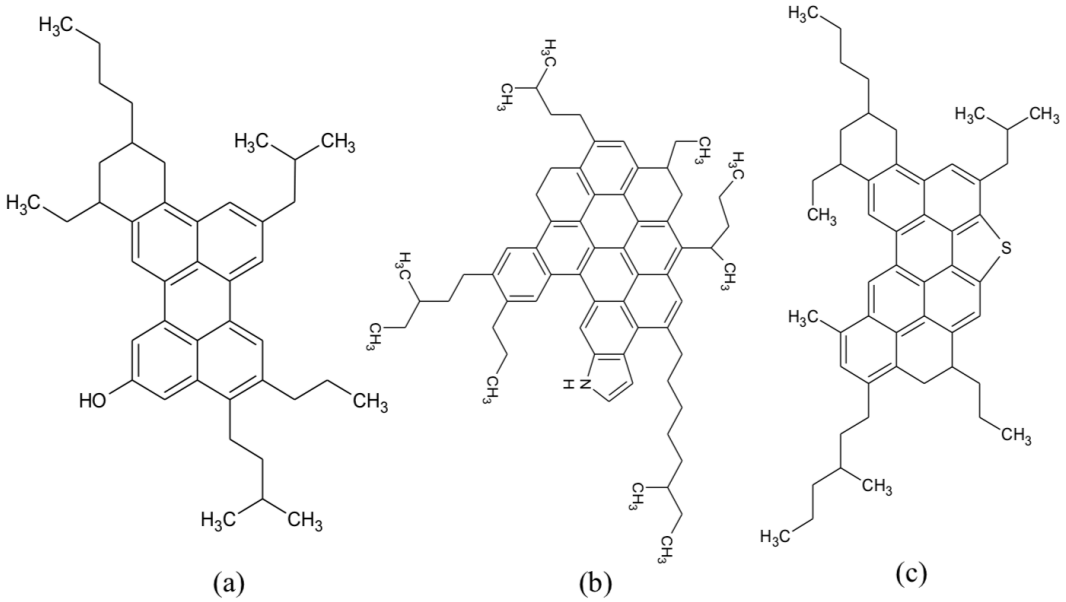


Figure 2.12. Asphaltenes: (a) asphaltene-phenol, (b) asphaltene-pyrrole, and (c) asphaltene-thiophene (Li and Greenfield 2014)

2.3.2 Bitumen in molecular dynamic simulation

Zhang and Greenfield (2009) used the preliminary method to analysis properties of bitumen such as density, viscosity and isothermal compressibility at different temperature by using the molecular dynamic (MD) analysis. The molecular dynamic results the viscosity and density decrease with the increased temperature. The MD results also showed the agglomeration of bitumen strongly relies on molecular composition of asphaltenes. According to the Zhang and Greenfield (2009) study, the Bhasin et al (2010) added a long polyethylene (PE) chain to one type of bitumen in order to investigate the physical property and mechanical property for the virgin bitumen and PE modified bitumen by using molecular dynamic simulations. The MD results showed the density of bitumen is higher than the unmodified bitumen and the isothermal compressibility of PE modified bitumen is much lower than the unmodified asphalt, which indicate the modified bitumen has a better mechanical and physical performance. The radial distribution function indicated increased aggregation of molecules of asphaltenes after mixing PE molecule.

Khabaz and Khare (2015) investigated the difference between the neat bitumen and styrene-butadiene rubber (SBR) in term of glass transition and molecular mobility by using the MD simulation. The results from radial distribution function showed increased aggregation of the asphaltene functions by presence of styrene-butadiene rubber (SBR). The glass transition and the mobility of constituent molecules were not seen to be different for modified bitumen and virgin bitumen.

Pan (2015) studied the cohesion and adhesion in the asphalt mixture using the molecular dynamic simulation. There are two types of aggregate (calcite and quartz) and one module of bitumen were used in the study. The results showed the cohesive energy within the bitumen is highly relied on the non-bonded energy between atoms and the adhesion bonding between the aggregate and bitumen dependent on the type of aggregate.

According the Pan's study (2015), Wang et al (2017) studied the effect of oxidised bitumen on adhesion at atomistic scale by using the MD simulation. Bitumen aging was modelled was built by converting to two resin molecules to an asphaltene molecule and one representative minerals (quartz) was used to represent the aggregate. He found the interfacial energy between the bitumen and aggregate is reduce by adding oxygen atoms. However, he also stated the result can only use to understand the adhesive bond energy at the bitumen-quartz interface.

Lemarchand et al. (2013) studied the adhesion between the oxidised bitumen and silicate mineral by using the MD method and atomic force microscopy (AFM) test. These two methods have been used to characterize the adhesion performance for neat, short-term aged and long-term aged asphalt mixtures. The number of molecules in the bitumen have been adjusted to conform to the experimental measurements of SARA fractions of neat bitumen and aged bitumen. The result demonstrated the additional oxygen atoms resulted more asphaltene fractions in the aged bitumen than virgin bitumen.

Yao et al (2016) investigated the effect of chemical aging on the properties of bitumen by MD simulation. They introduced carbonyl and sulfoxide function groups into the virgin bitumen to represent the aged bitumen. They found the aged bitumen has a higher density and viscosity values than the virgin

bitumen. They also indicated the additional carbonyl functions in the bitumen can result the better adhesion in the aggregate-bitumen system and also can improve the performance of moisture damage resistance in asphalt binder.

2.3.3 Low-density polyethylene (LDPE) in molecular dynamic simulation

Polyethylene (PE) is the most common plastic used widely in construction industry. Miller et al (2002) stated, according to the density and degree of molecular branching, the PE can be classified into three different types of PE, which are LDPE, medium-density polyethylene (MDPE) and HDPE, respectively. Frankland et al (2005) carried out MD simulations to study the chemical compositions of LDPE. The results showed the LDPE has a central backbone with many branches, and those branches also have branches. However, the results also indicated the lengths of all these branches are really difficult to determine. As a result, the structure and the chemical composition of LDPE are both hard to characterize.

According to the Frankland's study (2005), Zhang et al (2012) investigated the structure of LDPE using the MD simulation. As shown in the Figure 2.13, there are three types of LDPE have been classified based on the structure of LDPE. The first one has a single branch with CH_2 units (star-shaped), the second LDPE model has four branches with two branch sites at the end of backbone (H-shaped), The third one has four long branches with four branch sites randomly distributed along the backbone (comb-shaped). Zhang et al (2017) studied roles of branches, branch distribution and branch contents in the LDPE using the MD method. Three single models (see Figure 2.13) have been used to investigate the behaviours of LDPE. As a result, they found there are 100-600 CH_2 units in a single LDPE chain (backbone) and the branch contains 16 CH_2 units. They also noted that the comb shaped LPDE contains

more carbon atoms than other two types so that this structure can provided the better mechanical and physical properties.

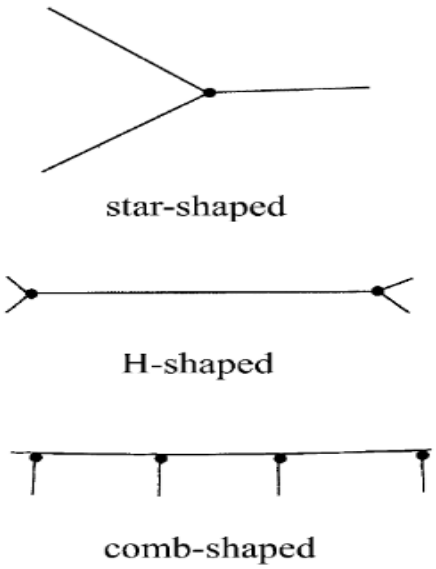


Figure 2.13 The schematic representing the three models of the polyethylene with well-controlled structure and long branching (Deng et al, 2015).

2.3.4 Aggregates in molecular dynamics simulations

Mineral rocks have been used in the road structure as aggregates. Pan et al (2015) stated that the compositions of the aggregate are very complex and has diverse mineralogical composition based on the chemistry. Wang et al (2015) investigated the most aggregate only contain one mineral or two mineral such as quartzite (SiO_2) and calcite ($CaCO_3$). The calcite is the prevalent elements in limestone; quartz is common in sandstones which contain a high percentage of silica. Li and Greenfield (2014) studied the effect of aggregate components on the adhesion between bitumen and surface of aggregate.

They selected CaO, MgO and Al_2O_3 to represent different mineral. The result showed the adhesion performance between aggregate and bitumen is highly depended on types of mineral. However, they also stated the result is quite different from reality as aggregate are always composed more than one mineral.

Li et al (2016) also investigated the effect of mineral types on the adhesion performance of bitumen-mineral system. In this study, quartz (SiO_2) and calcite(($CaCO_3$) were used to represent different minerals. The result indicated the interfacial adhesion performance between mineral and bitumen is mainly depended on the chemical property of mineral rather than the properties of bitumen. Gao et al (2018) investigated minerals can be classified into two main group, which are alkaline minerals and acidic minerals, respectively. Therefore, he decided to use four representative minerals instead of one simple mineral to build the interface. There has been a lot of research about asphalt by using MD.

2.4 Research Gap

In recent years, waste plastic such as LDPE have been introduced into the bitumen by using the wet process or dry process. McRebur claims plastic roads are better than traditional pavement in terms of lower maintenance cost and high engineering performance (McRebur,2018) in P38. Based on Zheng et al study, MD simulation is advantageous over the traditional laboratory-based method as it can help to understand the properties of bitumen at the molecular scale (Zheng.et al,2012) in P501. Gao et al summarised that the pavement performance is determined by the interfacial adhesion performance

between bitumen and aggregates (Gao et al,2018) in P70. In recent year, the MD simulation have been used to investigate the interfacial adhesion performance of asphalt binder.

Most of the research only focus on investigating the interfacial adhesion between aggregate and virgin bitumen using the MD simulation, and little work refers to the combined effect of LDPE and bitumen aging on the interfacial adhesion between bitumen and mineral at atomistic scale. Research into this field is limited because there are few researchers have used the MD simulation to understand the properties of LDPE when it is mixed with bitumen at molecular scale. The main aim of dissertation is to understand the combined effect of LDPE and oxidative aging on the interfacial adhesion between the bitumen and aggregate using MD simulations. Therefore, the model of virgin bitumen and modified bitumen are both constructed according to the saturate, aromatic, resin and asphaltene (SARA) four fractions. Two types of mineral substrates (quartz and calcite) are employed to construct bitumen-aggregate interfacial system. Finally, two main ways of introducing LDPE into bitumen: dry method and wet method are also simulated using molecular dynamics approach in the research. Therefore, this can help to understand if the adhesive bond energy of bitumen-mineral interface system can be affected by using two different processing method.

2.5 Literature Summary

To summarise, the literature reported the studies regarding the adhesion between the aggregate and bitumen component. Many present studies also indicated the LDPE modified bitumen can improve the properties of asphalt binder in terms of physical and engineering performance, which are favourable in road construction. The extensive literature reviews have examined two different processing methods

(e.g. wet process and dry process), which are generally used to incorporate the plastic into the bitumen. Also, most of the research also indicated the effect of asphalt oxidation on adhesion and cohesion at atomistic scale.

Finally, the fundamental purpose of the literature review is to increase knowledge in the LDPE modified bitumen and understand oxidative aging and chemical property of aggregate can both affect the interfacial adhesive energy between aggregate and bitumen. However, there is a lack of studies to evaluate the combined effect of oxidative ageing and LDPE on the interfacial adhesion performance between aggregate and bitumen. There are few researches investigate the combined effect of chemical property of mineral, oxidative aging and LDPE on the interfacial adhesion between the bitumen and aggregate. Therefore, the dissertation will attempt to fill in the gap in the literature and broaden existing knowledge.

CHAPTER 3 RESEARCH METHODOLOGY

3.1 Molecular Dynamic (MD) Theory

The molecular dynamic usually determines the trajectory of atoms or molecules in a system by integrating the motion of atoms. Yao et al（2016）applied the MD technique to simulate the instantaneous bitumen molecular behavior of the bitumen by elucidating the atomistic mechanisms which is used to determine the failure and deformation of interaction at nanoscale. The principle of MD simulation is the Newton's second law of motions and statistical mechanicals. Moreover, this method can be used to calculate the thermodynamic performance of the bitumen, in which the motion of each atom in the bitumen obeys the law of classical mechanics (F=ma).

Many force fields have been used to describe bitumen system in MD simulation. To understand the interatomic interactions, the condensed phase optimized molecular potential for atomistic simulation studies (COMPASS) force field is used in this study. This is because, the COMPASS force field is a simple and generic all-atom force filed to predict the interfacial interaction in the mixed system (Khabz et al.2015) in P10. The COMPASS force filed can also be expressed as superposition of valence interaction. Valence interaction is used to describe the types of interatomic interaction in atomistic modelling and calculate the potential energy between two atoms. Therefore, the potential energy usually consists of bond energy and non-bond energy as shown in the Eq. (1)

$$E = E_{bonded} + E_{non\text{-}bond} \quad (1)$$

Where E *bonded* is the bonded term for covalent interactions which is primarily include bond stretching, dihedral and improper interaction, E *non-bond* refers to the non-bonded pairs of atoms

which describes non-covalent contributions including van der Waals, electrostatic energy, and other energy (Martin-Martinez et al ,2015) in P109.

The van der Waals forces can be simulated by standard 12-6 Lennard Jones potential, which is attractive at large distances and repulsive once atoms are getting close together. The electrostatic interaction describes the interaction between the two charged atoms, which can be computed by coulomb interaction potential. There are some notable force fields have been applied in the molecular dynamic (MD) simulation, which are OPLS-AA, COMPASS, CHARMM and AMBER, respectively. The OPLS-AA force field is the all-atom optimized potential for liquid simulations which is a popular force field for simulating biomolecules. The Chemistry at Harvard macromolecular Mechanics (CHARMM) force field allows for generating and analyzing a wide range of molecular simulations. The most basic kinds of simulation are minimizing a given structure and production runs of a MD trajectory. The Assisted Model building with Energy Refinement (AMBER) force field is most used to simulate the biomolecules. However, each of these have different force constant and geometry parameters (Martin-Martinez et al ,2015) in P109. This study used COMPASS to predict dynamic organic and inorganic and interface systems because the COMPASS not only has a board coverage in covalent molecules such as organic material and also has coverage for the inorganic material such as metal and metal oxidize. This force filed (Compass force field) has been used successfully to simulate asphalt binder in other studies (Yao et al ,2016 in P10; Gao et al 2018 in P109).

3.1.1 Bonded interactions

The valence interactions include bond stretch (E_B), bond-angle bend (E_A), dihedral angle torsion (E_T), and inversion terms (E_I):

$$\mathbf{E_{val} = E_B + E_A + E_T + E_I} \quad \textbf{(2)}$$

For bond stretch and bond-angle bend interactions, COMPASS uses a harmonic distance form and a harmonic angle form, respectively:

$$\boldsymbol{E_B = \frac{1}{2}\sum_{bonds} k_{ij}^{bond} (r_{ij} - r_{ij}^0)^2} \quad \textbf{(3)}$$

Where, k_{ij}^{bond} is the bond stretch force constant, r_{ij} is the bond distance between atom I and atom j;

$$\boldsymbol{E_A = \frac{1}{2}\sum_{bends} k_{ijk}^{bend} (\theta_{ijk} - \theta_{ijk}^0)^2} \quad \textbf{(4)}$$

Where, k_{ijk}^{bend} is the bond-angle bend force constant, for two bonds ij and jk sharing a common atom, θ_{ijk} is the angle between bonds ij and jk, θ_{ijk}^0 is the equilibrium angle.

A dihedral angle is the angle between two intersecting planes. In chemistry, it is the angle between planes through two sets of three atoms, having two atoms in common. The dihedral angle torsion is defined as:

$$\boldsymbol{E_T = \frac{1}{2}\sum_{dihedrals} V_{jk}^{tor} \{1 - cos(n_{jk}(\varphi_{jk} - \varphi_{jk}^0)^2\}} \quad \textbf{(5)}$$

Where, V_{jk}^{tor} is the barrier to rotation, φ_{jk} is the dihedral or torsional angle between the ijk and jkl planes formed by two bonds ij and kl connected via common jk,$\varphi_{jk}^0$is the equilibrium angle.

The inversion potential is important for atoms that are bonded to three other atoms, which represents the favorability of keeping all the three bonds for atom i bonded to exactly three other atoms

j, k, and l, in the same plane. The inversion potential for normal planar configurations is expressed in cosine form:

$$\boldsymbol{E_I = \sum_{inversion} K_I^{inv} (1 - cos\psi_I)} \quad \textbf{(6)}$$

Where, K_I^{inv} is the inversion force constant, ψ_I is the angle between il bond and jik plane.

3.1.2 Non-bonded interactions

The energy interactions mentioned above, the non-bond interaction (E*nb*) is comprised of van der Waals (E_{vdw}) and Coulomb electrostatic (E_Q) interactions, as shown in the Eq (7)

$$\boldsymbol{Enb = E_Q + E_{vdw}} \quad \textbf{(7)}$$

- **Van der Waals Interaction**

The Van der Waals term is taken as sum of the intra and inter molecular attractive or repulsive interaction, which is the forces between the two atoms. The resulting Van der Waals can be calculated using the Lennard-Jones 9-6 potential:

$$\boldsymbol{E_{vdw} = \sum_{ij} \varepsilon ij \left[2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right]} \quad \textbf{(8)}$$

Where r_{ij} is the distance between atoms *i* and *j*. r_{ij}^0 and εij denote the distance between the interacting sites, the Lennard- Jones well depth, and the size parameter, respectively, for the pair of atom i and j.

- **Electrostatic Interactions**

The electrostatic interactions (EQ) describe the sum of Coulombic interaction between two charged atoms, as shown in the Eq (9)

$$\mathbf{E}Q = \sum_{i<j} \frac{Q_i * Q_j}{\varepsilon_{r*} R_{ij}} \quad \textbf{(9)}$$

Where Qi and Qj are atomic charges, Rij is the distance between atoms I and J, ε_r is the dielectric constant of the medium, respectively.

In this study, the MD simulation is conducted by Material Studio 7.0 software. All simulations in this study are performed at the temperature of 298k with a time step of 1fs. And the Ewald simulation technique are also used to apply for the electrostatic interaction. The atom-based summation with a cut-off distance of 15.5Å is applied for the interactions of van der Waals (Lu &Wang ,2011).

3.1.3 Ensembles

An ensemble is a collection of all possible microscopic states of a system that shares similar thermodynamic properties such as temperature and pressure. Molecular dynamic (MD) simulations are performed under different ensembles, based on the physical situation one intends to model. In order to analysis the trajectory of atoms and molecules in a system. The thermodynamic state of a system and microscopic state of a system should be defined. There are some small set of parameters including temperature, volume and pressure are usually used to represent the thermodynamic state of a system. The microscopic state of in a system can be defined by the positions of the atoms (Fired, 2007) inP4. Ensembles such as temperature and

volume can collect the all possible microscopic states in a system in order to share the similar thermodynamic properties (wang et al, 2004) in P10. According to the physical situation, the MD simulation can be performed under different ensembles which are microcanonical ensemble, canonical ensemble and isothermal-isobaric ensemble, respectively.

- **Microcanonical Ensemble**

In the microcanonical ensemble, the NVE is used to hold constant. N represents the number of particles; V represents the volume of the system and E is the total energy of the system. In this ensemble the system volume (V), the total energy of the system (E) and the number of particles (N) must remain constant throughout the whole simulation. And the average kinetic energy and temperature can vary in the microcanonical ensemble.

- **Canonical Ensemble**

In the canonical ensemble (NVT) the constant number of particles (N), volume of the system (V) and temperature (T) should remain constant throughout the simulation. This ensemble can be used to simulate a material subject to a constant volume experiment that with heat exchange with the environment.

- **Isothermal-isobaric Ensemble**

The isothermal-isobaric ensemble, NPT has constant number of particles (N), pressure in the system (P), and temperature in the system (T). This is equivalent to a constant atmospheric pressure which can exchange heat with the environment.

3.1.4 Constant temperature and pressure controls

Constant temperature and pressure conditions in molecular dynamics simulations are enforced using thermostats and barostats. In this study, Andersen and Nose-Hoover algorithms are used to main a constant pressure and a constant temperature, respectively.

- **Nose Hoover-Langevin (NHL) thermostat**

In this study, the temperature control can be achieved by Nose-Hoover algorithm. To control a constant temperature, Hoover (1980) developed a system to couple with a heat bath, allowing heat to be transferred back and forth between the system and heat bath.

- **Andersen barostats**

Andersen (1980) thermostat describes a physical system with weak stray interactions between the molecules in the system and the particles of a heat bath at a specified temperature. A stochastic method is implemented, where the collision to the imaginary heat bath is simulated via resetting the velocity of a randomly selected atom from the Maxwell-Boltzmann distribution at a certain predefined interval.

The time between collisions is chosen from a Poisson distribution with a certain average collision time. When the collision interval is large, energy fluctuations will occur slowly along with the kinetic energy fluctuations simulating that of a conventional MD. If the collision interval is too small, the kinetic energy fluctuations could be too high and that in turn could slow down the speed at which the molecules in the system explore the configuration space. According to the extended system, Andersen (1990) developed a system to keep the pressure in constant. This system is coupled to an external

variable which is the volume of volume. This system can simulate the action of a piston on a real system, which is a three- dimensional (3D) virtual piston.

3.1.5 Work of adhesion from MD simulations

In order to analysis the adhesion between the bitumen and mineral, the work of adhesion can be used to characterize the adhesive bond energy. The work of adhesion reflects the interfacial adhesion strength which required separating a unit area of the bitumen-mineral interface into the surface of bitumen and surface of mineral. In the Material Studio (MS) 7.0, as shown in the Equation (10)-(11), the total adhesive energy between the mineral and the bitumen can be obtained by calculating the potential energy of bitumen and the potential energy of mineral (Van Gunsteren,2019).

$$\mathbf{E\ adeshion = E_{total} - (E_{bitumen} + E_{mineral})} \quad \mathbf{(10)}$$

$$\mathbf{W_{adhesion} = E/A} \quad \mathbf{(11)}$$

Where is the interfacial energy between bitumen and mineral; E_{total} is the total potential energy of bitumen-mineral system, $E_{bitumen}$ represents the potential energy of bitumen and $E_{mineral}$ represents the potential energy of mineral, $W_{adhesion}$ is the work of adhesion of the interface between the bitumen and aggregate, and A is the contact area between surface of mineral and the surface of bitumen.

Gao. et al (2018) stated the total potential energy included valence bond and non-bond energy. Valence bond energy generally consists of out-of-plane bending and bond

extensibility. As shown in the Equation (2), Non-bond energy consists of van der Waals energy and Coulomb electrostatic energy. In this study, the adhesive energy of bitumen-mineral system is only made up of non-bond energy after calculation. In this study, all the simulation results of interfacial energy between the bitumen and mineral are positive which means there is a strong mutual attraction between the bitumen and the mineral. Moreover, in this study, the higher value of E represents the better interfacial adhesion performance between aggregate and bitumen.

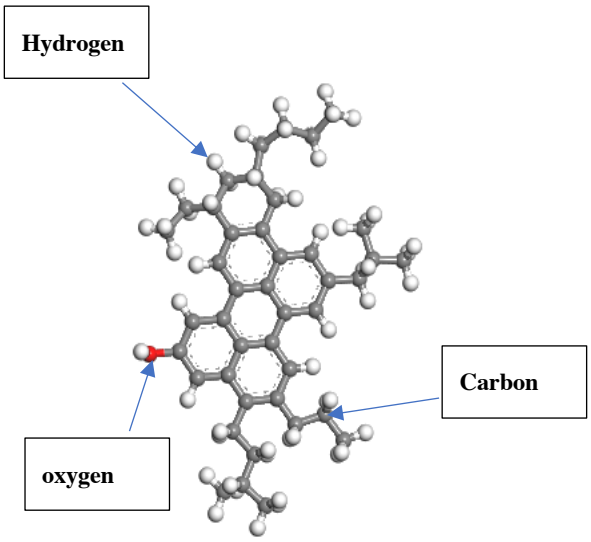
3.2 Building Component Molecular Models

3.2.1 Modelling virgin bitumen components

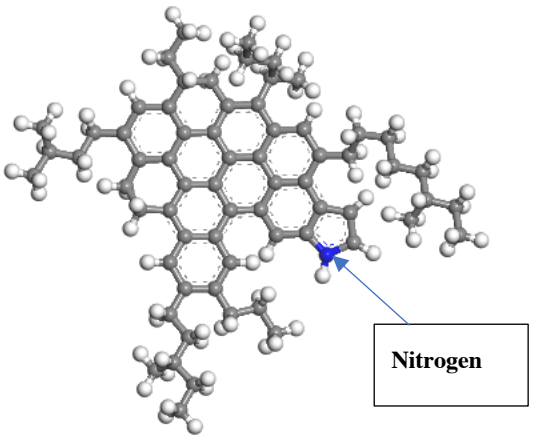
According to the studies by Li and Greenfield (2013) and Martin-Martinez et al (2015), the virgin bitumen model was built by using the propositions in those two studies. Therefore, the models proposed in those two studies were used to build the bitumen models without adding oxygen. The asphaltenes and saturate molecules are taken from Li and Greenfield (2013). The aromatic and resins molecules are taken from Martin-Martinez et al (2015). Figure 3.1 to Figure 3.4 show the molecular structure of asphaltenes, saturate, aromatic, and resins molecules respectively. As can be seen from the figures, the black atoms are carbons; the white atoms are hydrogen; the red atoms are oxygens; the yellow atoms are sulfurs and the blue atoms are nitrogen.

- **Asphaltenes**

AS-1



AS-2



AS-3

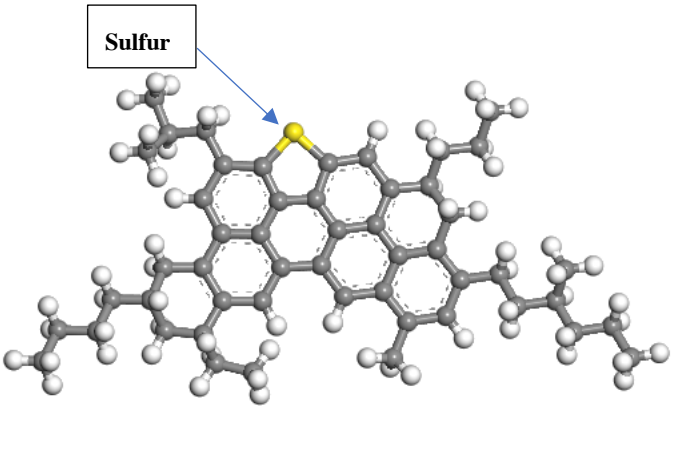
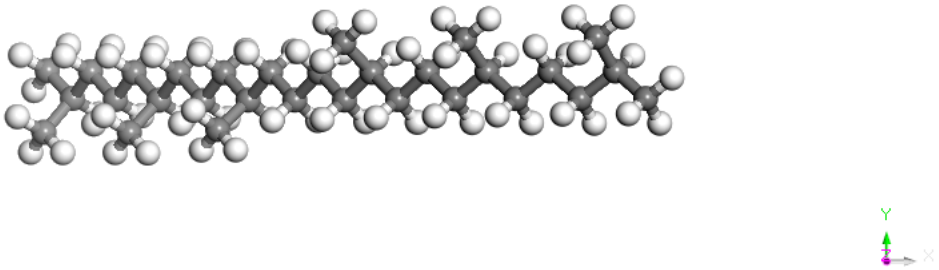


Figure 3.1 ***Molecular structures of asphaltene fraction: AS-1 asphaltene-phenol, $C_{42}H_{54}O$, AS-2 asphaltene-pyrrole, $C_{66}H_{81}N$, and AS-3 asphaltene-thiophene, $C_{51}H_{62}S$ (Li and Greenfield 2014).***

- **Saturate**

SA-1



SA-2

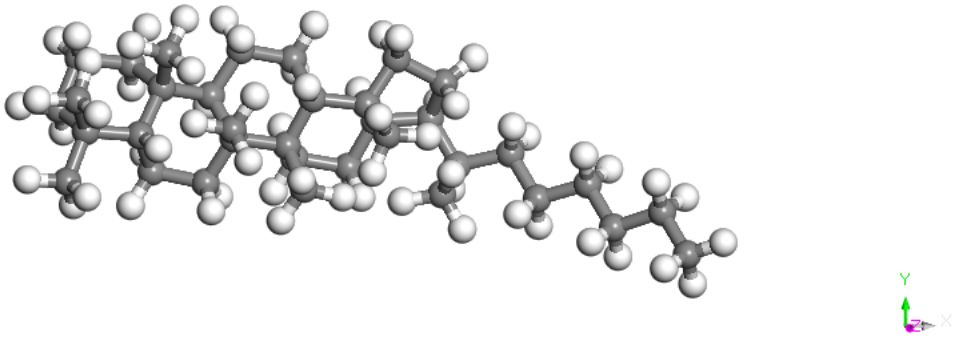
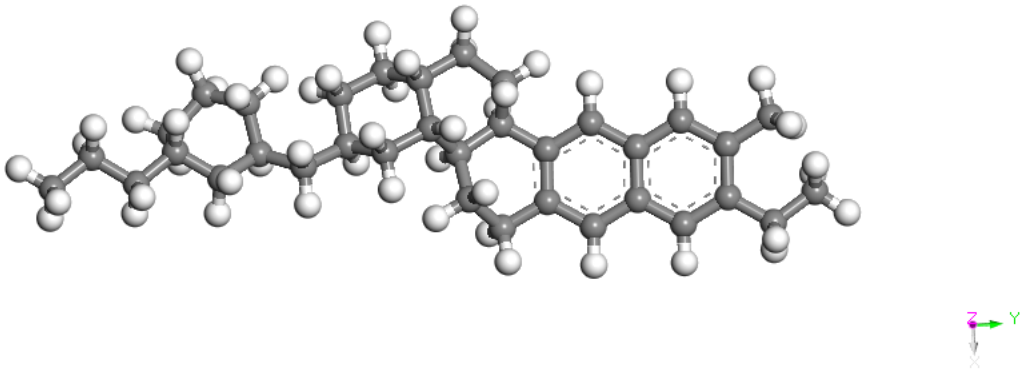


Figure 3.2 Molecular structures of saturate fraction SA-1, squalane; SA-2, hopane.

- **Aromatic**

AR-1



AR-2

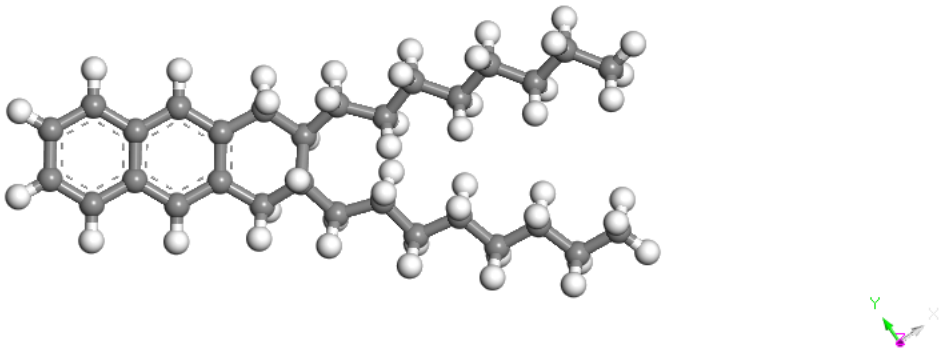
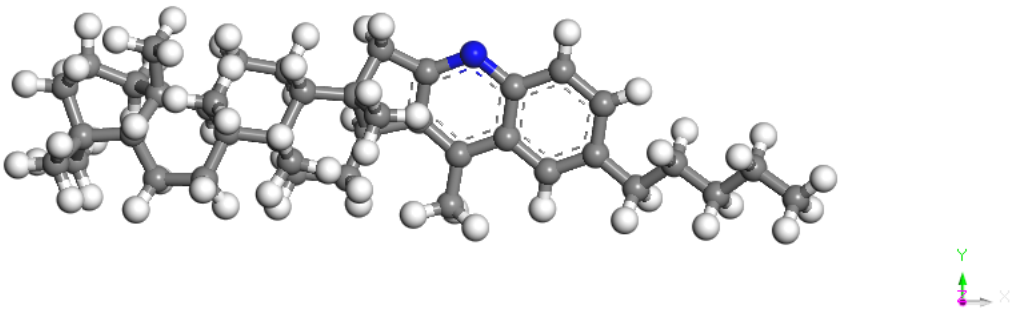


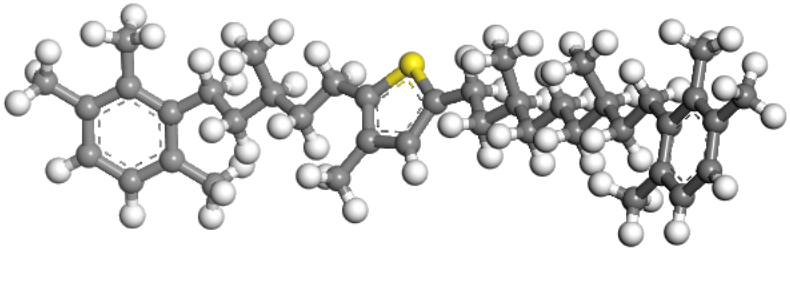
Figure 3.3. Molecular structures of aromatic fraction (AR-1, PHPN; AR-2, DOCHN)

- **Resins**

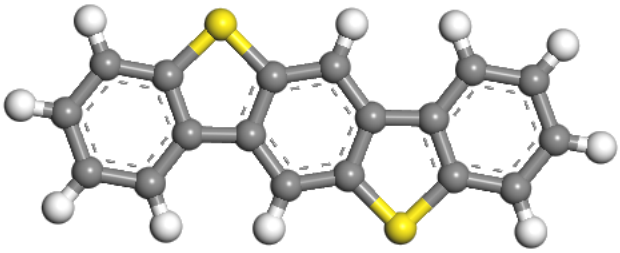
RE-1



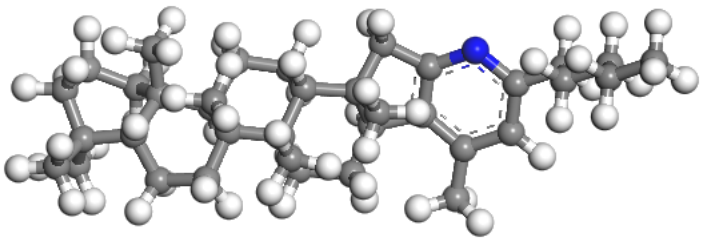
RE-2



RE-3



RE-4



RE-5

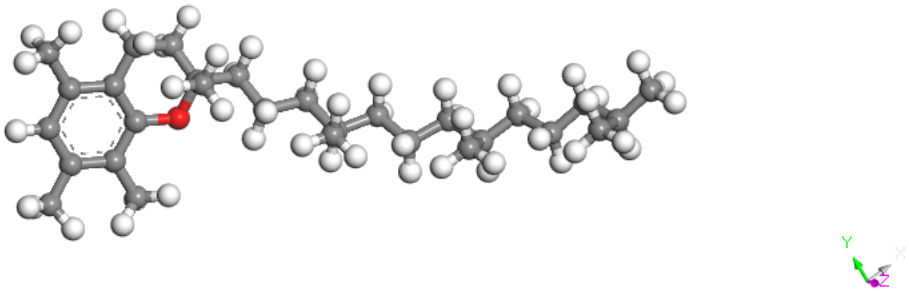


Figure 3.4. Molecular structures of resin fraction RE-1, quinolinohopane; RE-2, thioisorenieratane; RE-3, benzobisbenzothiophene; RE-4, pyridinohopane; RE-5, trimethylbenzeneoxane.

3.2.2 Modelling Oxidized Bitumen Components

As previously stated, the oxidized bitumen molecules were developed by introducing additional oxygen atoms into its existing sensitive chemical functional groups. Therefore, as shown in the Figure 3.5 there are two oxidative products have been formed in bitumen system after aging: One is ketones formed at benzylic carbon atoms which adjacent to aromatic ring systems, and sulfoxides formed at sulfide (Pan et al ,2010). As a result, there are different number of oxygen atoms were added to the different sensitive function group. Peteresen (2009) found when adding more oxygen atoms into the virgin bitumen system, there are few asphaltene molecules changed to resins, and resins fraction changed to the aromatics. However, the fraction of saturate have no change as it does not contain any sensitive functional groups.

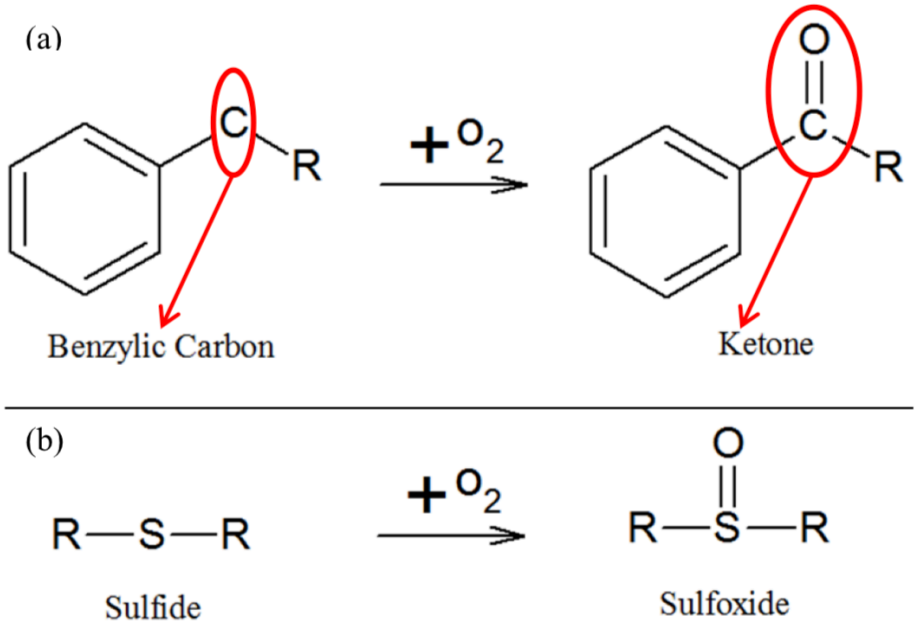
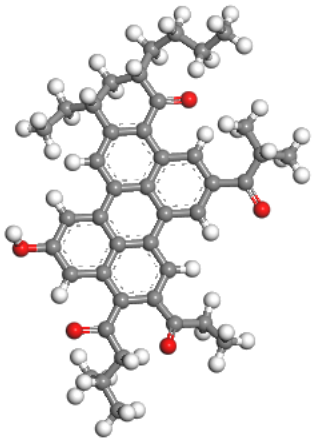


Figure 3.5 Oxidation of sensitive function groups in the virgin bitumen (a) formation of ketone and (b) formation of sulfoxide (Pan and Tarefder,2016).

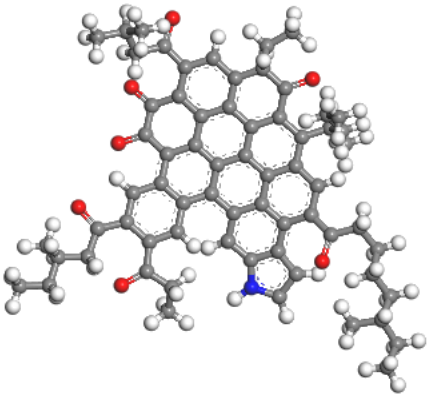
Based on the stated as above, the fraction of aromatics, resin and asphaltenes in the bitumen have been developed by adding oxygen atoms into sensitive functional groups. As can be seen from Figure 3.6 to Figure 3.8 as below, the ketones and sulfoxides have been created after oxidative aging in each bitumen molecule. And the saturates have no changes after aging due to no sensitive function groups within it.

- **Oxidized Asphaltenes**

AS-1



AS-2



AS-3

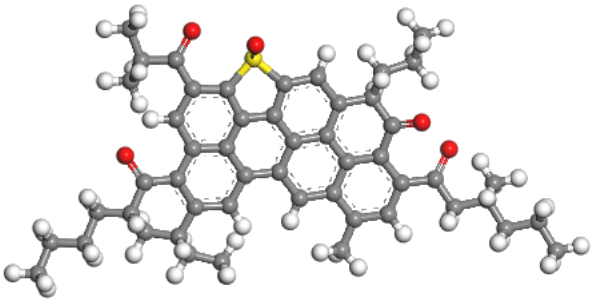
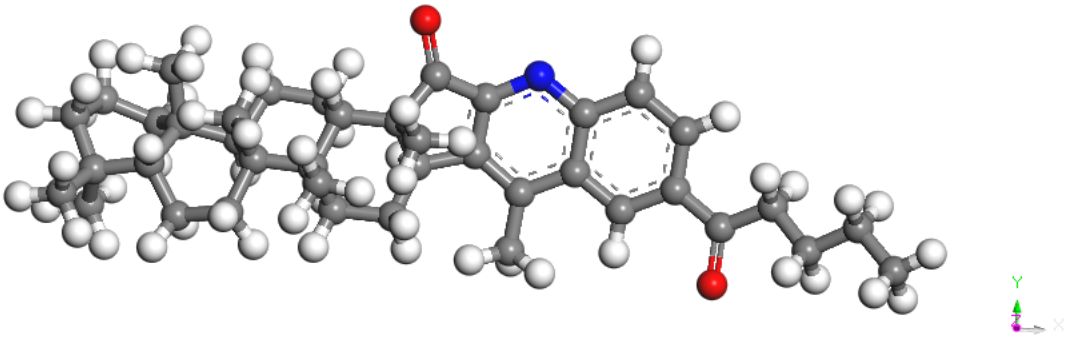


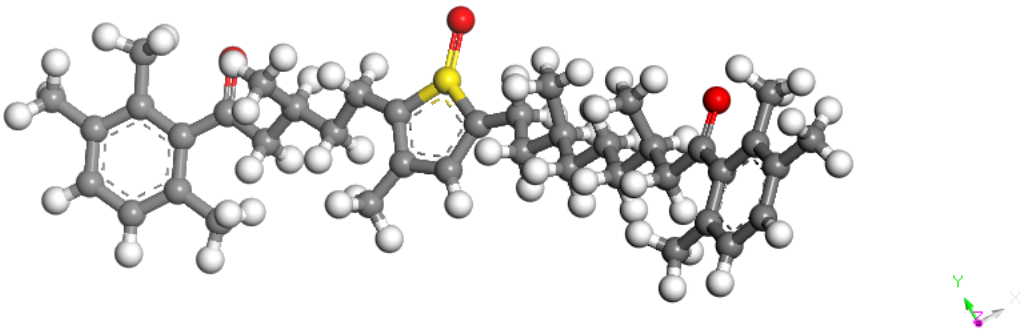
Figure 3.6. Asphaltene fraction after oxidative aging: (a) oxidized asphaltene-phenol, $C_{42}H_{46}O_5$, (b) oxidized asphaltene-pyrrole, $C_{66}H_{67}NO_7$, and (c) oxidized asphaltene-thiophene, $C_{51}H_{54}SO_5$

- **Oxidized Resins**

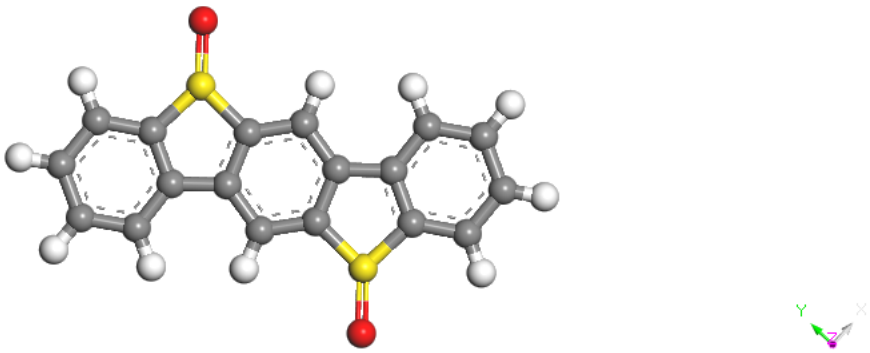
RE-1



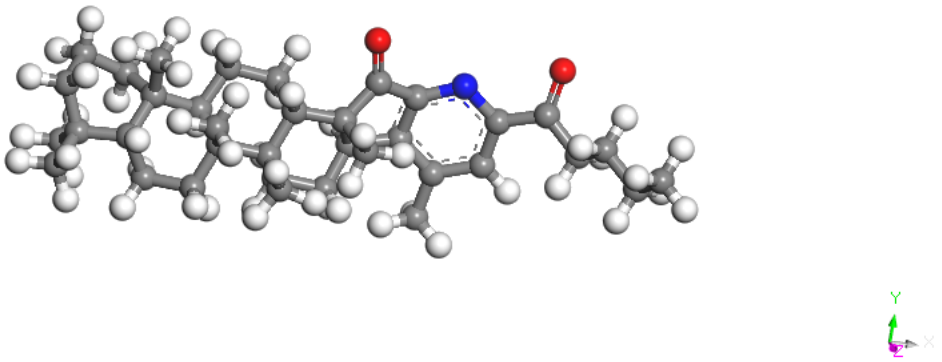
RE-2



RE-3



RE-4



RE-5

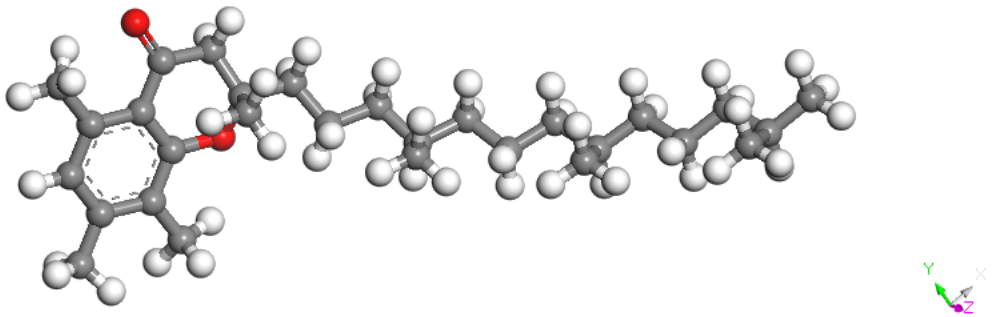
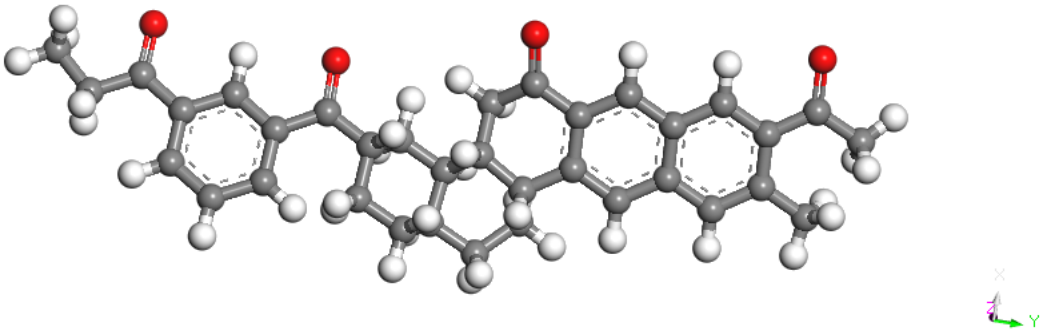


Figure 3.7. Resin fraction after oxidative aging: (a) oxidized quinolinohopane, $C_{40}H_{55}NO_2$, (b) oxidized pyridinohopane, $C_{36}H_{53}NO_2$, (c) oxidized benzobisbenzothiophene, $C_{18}H_{10}S_2O_2$, (d) oxidized trimethylbenzene-oxane, $C_{29}H_{48}O_2$, and (e) oxidized thio-isorenieratane, $C_{40}H_{56}SO_3$

- **Aromatic**

AR-1



AR-2

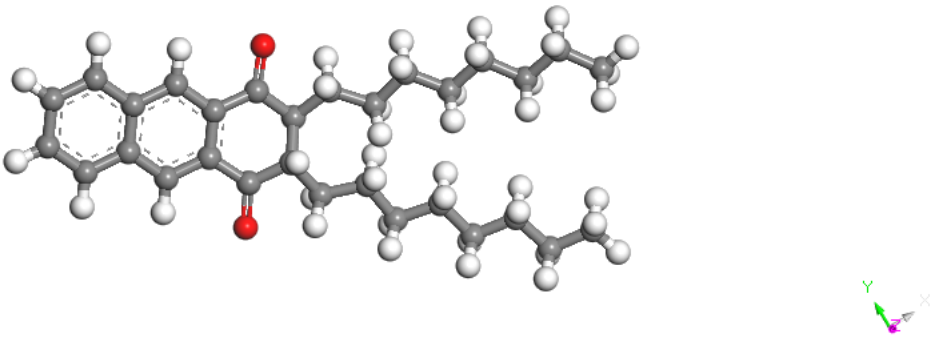


Figure 3.8 Aromatic fraction after oxidative aging: (a) oxidized PHPN, $C_{35}H_{36}O_4$ and (b) oxidized DOCHN, $C_{30}H_{42}O_2$

3.2.3 Modelling Low-density of polyethylene (LDPE) components

Based on the investigation from Zhang et al (2002), a LDPE molecule usually contains 100-500 CH_2 units under the temperature 300k. As stated in the Section 2, some studies have stated that the low-density polyethylene (LDPE) is a highly branched structure. There are three common structures have been used in the MD, which are star shaped LDPE, H shaped LDPE and comb shaped LDPE, respectively (see Figure 2.13). Few studies have shown the

comb-shaped LDPE has a better performance than other two types, so the comb-shaped LDPE has been widely applied in the molecular dynamic (MD) simulation (Moyassari et al, 2019). Sun.et al (2019) stated the length of branch in the LDPE cannot up to 16 carbon atoms as it could cause the co-polyethylene crystallization.

In order to simulate a well-structured LDPE, a comb-shaped LDPE with 160CH_2 units is used in this study. Due to the structure of comb -shaped LDPE molecule has been presented by Sun et al (2019), the structure of comb-shaped LDPE molecule in this study is used in this study. Figure 3.7 shows the backbone of comb-shaped LDPE contains 130CH_2 units and two branches site randomly distributed along the backbone, each branch contains 15 CH_2 units. The black sticks represent the carbon atoms and the white sticks are hydrogen atoms (see Figure 3.7).

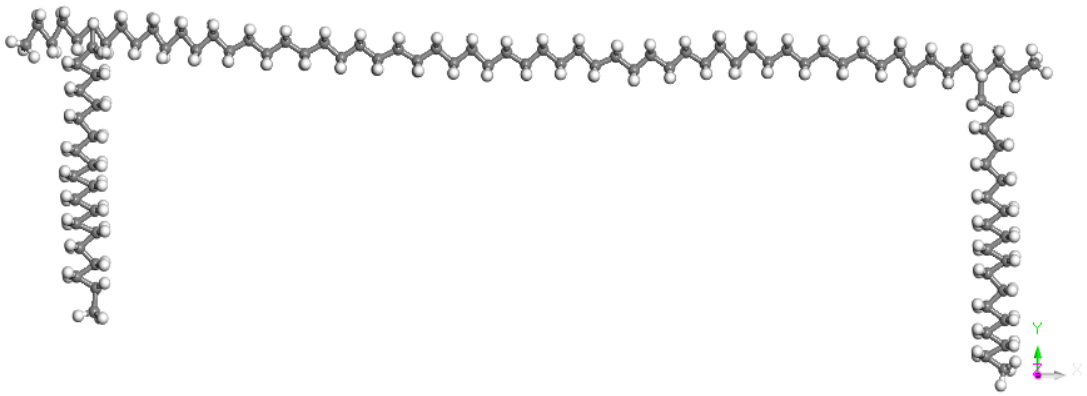


Figure 3.7 The model of comb-shaped low-density polyethylene (160CH_2 units) with two branches.

3.3 Building System Molecular Model

3.3.1 Parameter setting in molecular dynamics simulations

According to the investigation from Rakesh (2009), different parameters such as pressure temperature, cutoff radius and simulation time step could all affect the simulation results. Therefore, in this study, system temperature was set at 298k under the pressure of 1.0atm (101.325 kPa). The smooth particle mesh Ewald (SPME) method is used for handling long-range electrostatic and van der Waals interactions.

In order to minimize the effect of cutoff radius on the simulation result, the cutoff was considered as 15.5Å so that two atoms cannot meet two copies of another atom or other molecules (Lu& wang.2011). Moreover, the time of simulation was set as 1.0 fs time step and with simulation duration of 200 Ps (200,000 running step) for all the simulation. An isothermal-isobaric ensemble, also called NPT ensemble, was then used to simulate the realistic asphalt systems and to obtain the densities of asphalt systems. The simulation time step under the NPT ensemble was set at 1 fs with simulation duration of 200 ps (200,000 running steps) to guarantee the system could reach equilibrium.

3.3.2 Bitumen system modelling

Based on Li and Greenfiled's (2014) study, they proposed the SHRP AAA-1 model bitumen is the closet to the real bitumen molecule. As a result, this model is selected for this study. To understand the combined effect of LDPE and oxidative aging on adhesion performance between mineral and bitumen, the virgin bitumen, pressure aging vessel (PAV) aged virgin bitumen, LDPE modified virgin bitumen and pressure aging vessel aged LDPE modified

bitumen are selected to analysis in the study. The SARA mass fractions and LDPE content for each model are shown in the Table 4.

Table 4. SARA mass fractions and LDPE content of four bitumen model systems.

Virgin bitumen		**PAV aged virgin bitumen**		**LDPE modified unoxidized bitumen**		**LDPE modified oxidized bitumen**	
component	%content	Component	%content	Component	%content	Component	%content
Saturate	10.7	Saturate	10.7	Saturate	9.45	Saturate	9.45
Aromatics	38.1	Aromatics	37.3	Aromatics	36.85	Aromatics	35.95
Resins	30.6	Resins	31.1	Resins	29.35	Resins	29.85
Asphaltenes	16.5	Asphaltenes	16.9	Asphaltenes	15.25	Asphaltenes	15.65
				LDPE	5	LDPE	5

As can be seen from Table 4, the mass percentage of Asphaltenes fractions is decreased after the aging process. This can indicate that the more polar fractions are formed in the asphalt after aging. The aim of this study is to understand the combined effect of both oxidative aging and additional LDPE on the cohesive energy of virgin bitumen. Therefore, the LDPE (9%) molecules is introduced into both virgin bitumen model and oxidized bitumen model. Based on the bitumen model developed by Li and Greenfiled (2014), the number of each type of molecules have been developed so that the content of LDPE can be achieved 9% for each model. The actual number of each fraction for each model has been shown in Table 5.

Table 5. Molecular composition for each bitumen system model (VB[a]-Virgin bitumen, OB[b]- Oxidised bitumen, LMVB[c]-LDPE modified virgin bitumen, LMOB[d]-LDPE modified oxidized bitumen.)

Molecules in model		Molecular formula	Number of molecules			
			VB[a]	OB[b]	LMVB[c]	LMOB[d]
Saturate	Squalane	$C_{30}H_{62}$	8	8	8	8
	Hopane	$C_{29}H_{50}$	8	8	8	8
Aromatic	PHPN	$C_{35}H_{44}$	22	0	22	0
	Oxidised PHPN	$C_{35}H_{36}O_4$	0	22	0	22
	DOCHN	$C_{30}H_{46}$	26	0	26	0
	Oxidised DOCHN	$C_{30}H_{42}O_2$	0	26	0	26
Resin(polar aromatic)	Quinolinohopane	$C_{40}H_{59}N$	8	0	8	0
	Oxidised Quinolinohopane	$C_{40}H_{55}NO_2$	0	8	0	8
	Thioisorenieratane	$C_{40}H_{60}S$	8	0	8	0
	Oxidised Thioisorenieratane	$C_{40}H_{56}SO_3$	0	8	0	8
	Benzobisbenzothiophene	$C_{18}H_{10}S_2$	30	0	30	0
	Oxidised Benzobisbenzothiophene	$C_{18}H_{10}S_2O_2$	0	30	0	30
	Pyridinohopane	$C_{36}H_{57}N$	8	0	8	0
	Oxidised Pyridinohopane	$C_{36}H_{53}NO_2$	0	8	0	8
	Trimethylbenzene-oxane	$C_{29}H_{50}O$	10	0	10	0
	Oxidised Trimethylbenzene-oxane	$C_{29}H_{48}O_2$	0	10	0	10
Asphaltene	Asphaltene-phenol	$C_{42}H_{50}O$	6	0	6	0
	Oxidised Asphaltene-phenol	$C_{42}H_{46}O_5$	0	6	0	6
	Asphaltene-pyrrole	$C_{66}H_{81}N$	4	0	4	0
	Oxidised Asphaltene-pyrrole	$C_{66}H_{67}NO_7$	0	4	0	4
	Asphaltene-thiophene	$C_{51}H_{62}S$	6	0	6	0
	Oxidised Asphaltene-thiophene	$C_{51}H_{54}SO_5$	0	6	0	6

Low-density polyethylene	LDPE	CH_2	0	0	5	5

Firstly, all the unoxidized bitumen molecules are placed into a cubic simulation box and the initial density is set as 0.1g/cm^3 so that all unoxidized bitumen molecules can be distributed randomly in the cubic box. In order to remove all non-bonded overlapping between different molecules, the virgin bitumen system model is obtained along with a geometry optimization process. In this process, the COMPASS force field is conduced to minimize the system energy with 5000 interactions. Thereafter, an isothermal-isobaric ensemble, which called NPE ensemble is also used for the simulation for 200ps with 1.0fs time steps (200,000 running steps). This process can make the amorphous bitumen system to close the realistic bitumen system and to obtain the realistic densities of virgin bitumen system. Finally, the canonical ensemble (NVT) is used to guarantee the virgin bitumen model can be reached an equilibrium. The duration of simulation is set as 200ps with 1.0fs (2,000,000 running steps).

All the MD simulations are performed under the 298K temperature and a pressure of 101.325 kPa (1.0atm) and the size of simulation box is selected 100×100×100Å^3 so that it is large enough to contain all the molecules. For the aged unmodified bitumen model, all oxidized components (see Table 5) will be assigned in this model. And the aged virgin bitumen model is built by following the same procedure as the virgin bitumen model.

According to John (2006) study, LDPE modified asphalt using the wet process can be produced by mixing the LDPE into the bitumen directly. Therefore, in order to simulate the model of LDPE modified virgin bitumen and model of LDPE modified oxidized bitumen, the extra five LDPE

molecules is introduced into the two different models, respectively. Therefore, the unoxidized and the oxidized components are placed into their individual simulation box with five LDPE molecules (9% weight) to represent LDPE modified unoxidized bitumen model and LDPE modified oxidized bitumen model. The method of MD simulation for these two modules are following same procedure as the virgin bitumen model bitumen system. Figure 3.9 shows the four-final structure of model bitumen systems after NPT simulation.

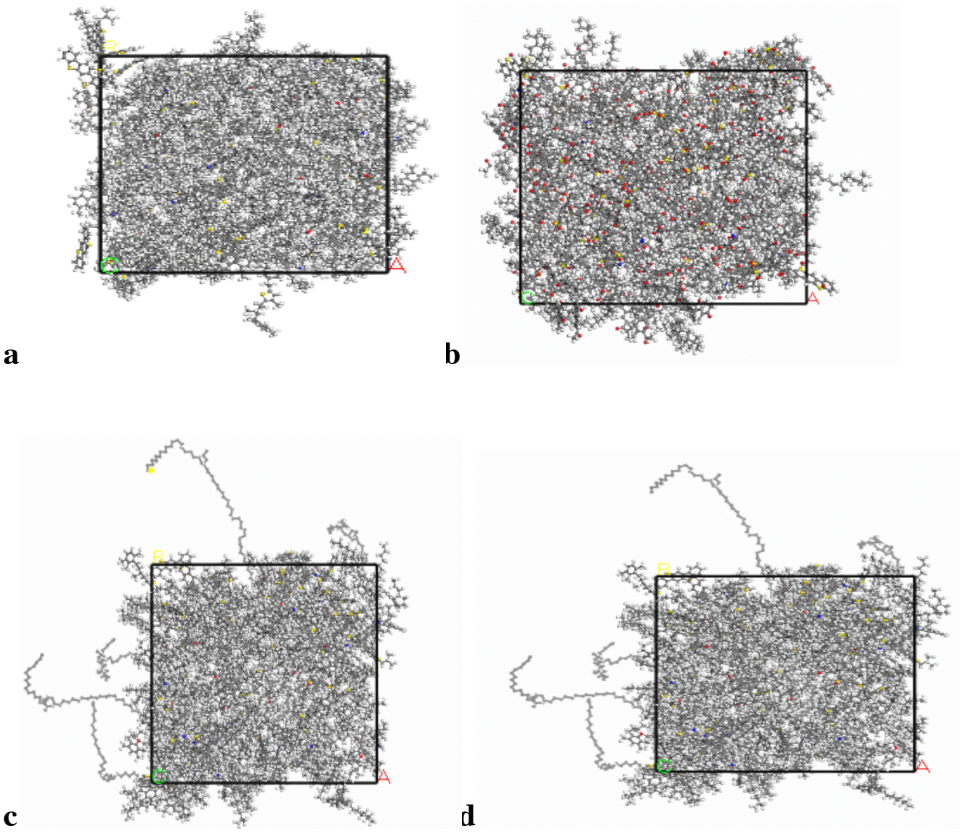


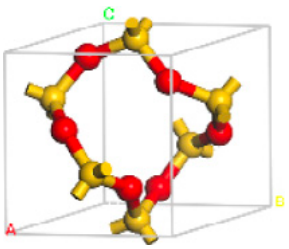
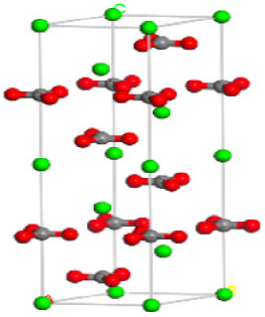
Figure 3.9 Four models built for MD simulation (a) Virgin bitumen model, (b) oxidized unmodified bitumen model (c) LDPE modified virgin bitumen model (d) LDPE modified oxidized bitumen model.

3.3.3 Aggregate System Modelling

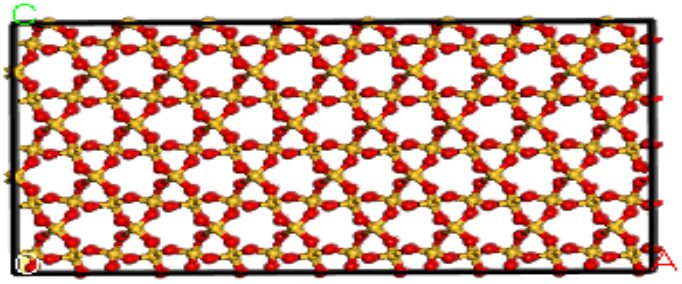
According to the stated in the chapter 2, The aggregate has been widely used in the pavement industry. Based on the chemistry, mineralogy and petrology, Aggerates have diverse mineralogical composition. Deng et al (2012) investigated the interfacial adhesive energy between the aggregate and bitumen highly relies on the chemical composition of aggregate. Some aggregate has high purity as they only contain one type of mineral such as quartz (SiO_2) or Calcite ($CaCO_3$). However, there are few aggregates which contain more than one types of mineral. Tombacz (2002) summarized that each mineral has unique chemical composition so that there are non-polar and polar active sites on different types of minerals.

Miller et al (2012) stated there are eight common chemical elements in the aggregate which are oxygen, silicon, aluminum, iron, calcium, sodium, potassium and magnesium. Natural mineral is normally crystalline, and the crystal structure of mineral depends on the internal atomic arrangement. The crystal structure of mineral can influence the performance of aggerate as it affects the mineral's property. In this study, the quartz and calcite are selected as these two types of mineral which is generally existing in the aggregate and present polar active sites or non-polar active sites. In this study, all selected minerals are performed in a box called unit cell. The box includes the six lattice parameters (length a, b, c and angle) and chemical components (Oxygen, Silica, Carbon and Calcium). Table 6 shows the six lattice parameters for these two representative minerals.

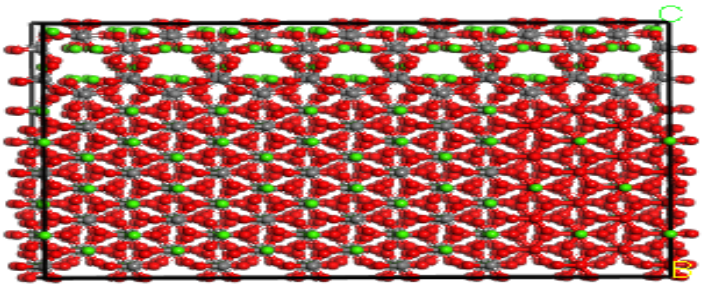
Table 6 The six parameters of two minerals in MD simulation

Minerals	**Unite cell structure**	**Lattice parameters**	**Chemical formula**
Quartz		a = b = 4.910 Å, c = 5.402Å a = b = 90, c = 120	SiO_2
Calcite		a = b = 4.990 Å, c = 17.046Å a = b = 90, c = 120	$CaCO_3$

To construct the mineral supercell, the bulk crystal is first inserted and cleaved along Miller plane to expose the surface for quartz and calcite. Secondly, the geometry optimization is conducted first and the mineral surface is realized and extended to create two-dimension (2D) structure by repeating the number of unit cell in x and y direction. Moreover, a vacuum layer of 0 Å is included above the extended surface of mineral to create a mineral block called supercell so that the supercell can be presented with periodic boundary condition. Figure 3.10 shows the details for two mineral system models.



a



b

Figure 3.10. two mineral model used for the simulation (a). Quartz a=54.67, b=64.12 c=21.9. (b). Calcite a=b=53.26, c=23.9.

3.4 Building Bitumen-Mineral Interface Molecular Models

In this study, there are twelve different bitumen-mineral interface systems are built in order to understand the following aims of this study:

1. The effect of oxidative aging on work of adhesion between aggregate and bitumen.
2. The effect of LDPE processed by dry and wet methods on work of adhesion between aggregate and bitumen.
3. Combined effects of LDPE and oxidative aging on bitumen-mineral interfacial adhesion using the two processing methods.

Therefore, based on the aims of this study, these twelve systems can be further subdivided into three groups.

3.4.1 Virgin or oxidized bitumen-mineral interface systems

To construct the virgin or oxidized bitumen-mineral interface system, a confined layer of bitumen is built with the same width and length as the mineral layer. And then, for the model construction, a confined layer of virgin or oxidized bitumen model is combined with mineral layer by using 'build layer' tool and then a vacuum layer with thickness 70Å is added on the top of bitumen layer to avoid interaction across the mirror image in the z-direction.

To establish the layer structure, calculation the geometry optimization is very necessary. The main reason is the mineral surface and bitumen layer have been optimized but the confined layer of mineral is constrained as it is not optimized. After geometry optimization process, the bitumen-mineral interface system has reached stability and electron energy minimization. And then, the interface system is subjected to NVT equilibration with additional 200ps for further trajectory analysis and calculation. The duration of simulation is demonstrated to be sufficiently long and the trajectory files are used to calculate the adhesive energy between bitumen layer and mineral layer after the NVT simulation. After NVT simulation, there are 20 frames are output as there are one frame is outputted with an average of 10ps. All the simulations in this study are performed under 298k with a step of 1.0fs. The four-interfaced bitumen-aggregate systems are illustrated in Figure 3.11.

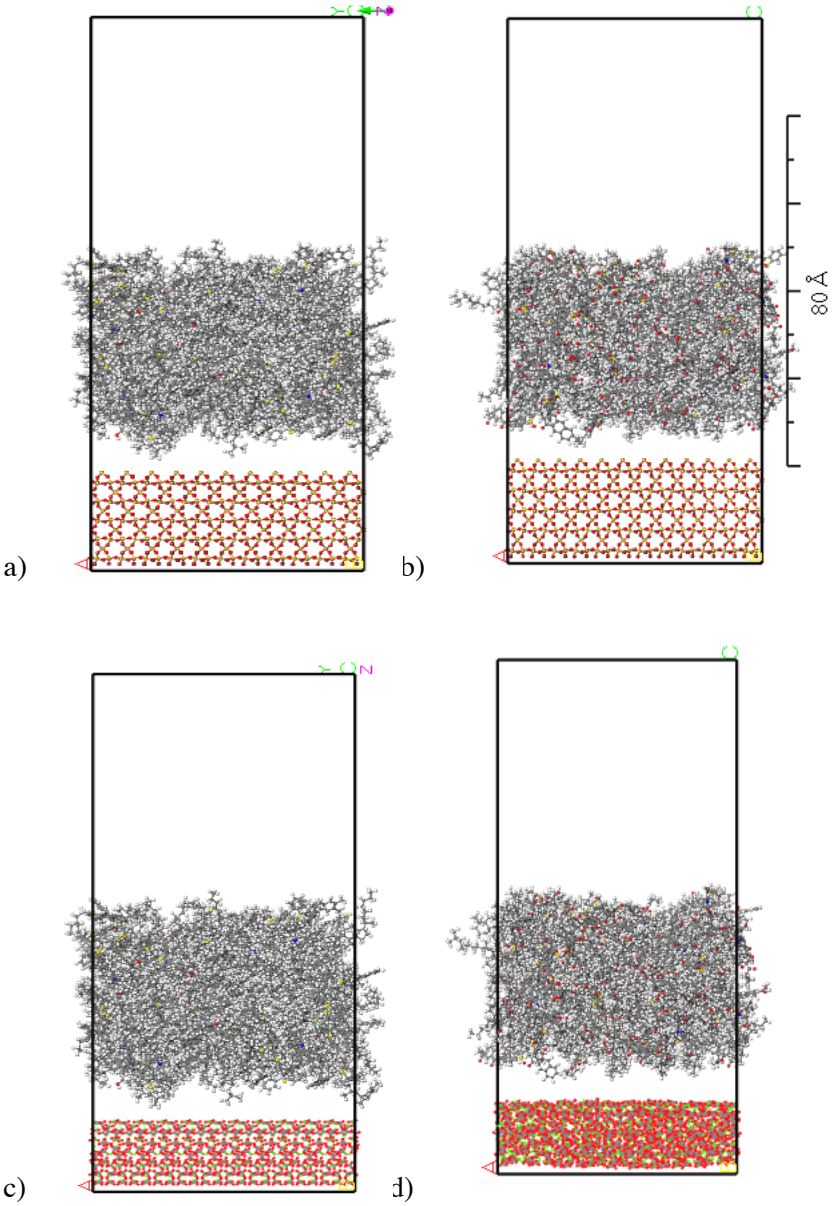


Figure 3.11 the virgin or oxidized bitumen-mineral interface systems (a) the virgin bitumen-quartz model, (b) the oxidized bitumen-quartz model, (c) the virgin bitumen-Calcite model, (d) the oxidized bitumen-calcite model.

3.4.2 LDPE modified virgin or oxidized bitumen-mineral interface systems - wet process

For understanding the LDPE modified aged bitumen and LDPE modified virgin bitumen (wet mixing process), there are four bitumen-mineral system models have been constructed. As stated in the section 3.6, the five LDPE molecules (9% weight) are added into either oxidized bitumen model or virgin bitumen model to create two confined layers which are LDPE modified virgin bitumen confined layer and LDPE modified aged bitumen confined layer, respectively. Once the LDPE-bitumen layers are built, these two confined layers are subjected to a geometry optimization with NVT ensemble in order to equilibrate the system.

The bitumen-LDPE layer is constructed with the same length and width as the confined layer of mineral. As mentioned above, a vacuum layer is placed upon the top of the confined layer of modified bitumen or modified oxidized bitumen. Finally, the LDPE modified bitumen-mineral system and LDPE modified aged bitumen-mineral system are both following the same steps as the unmodified bitumen-mineral systems. Figure 3.12 shows the four different models for LDPE modified virgin layer or LDPE modified aged bitumen with two minerals.

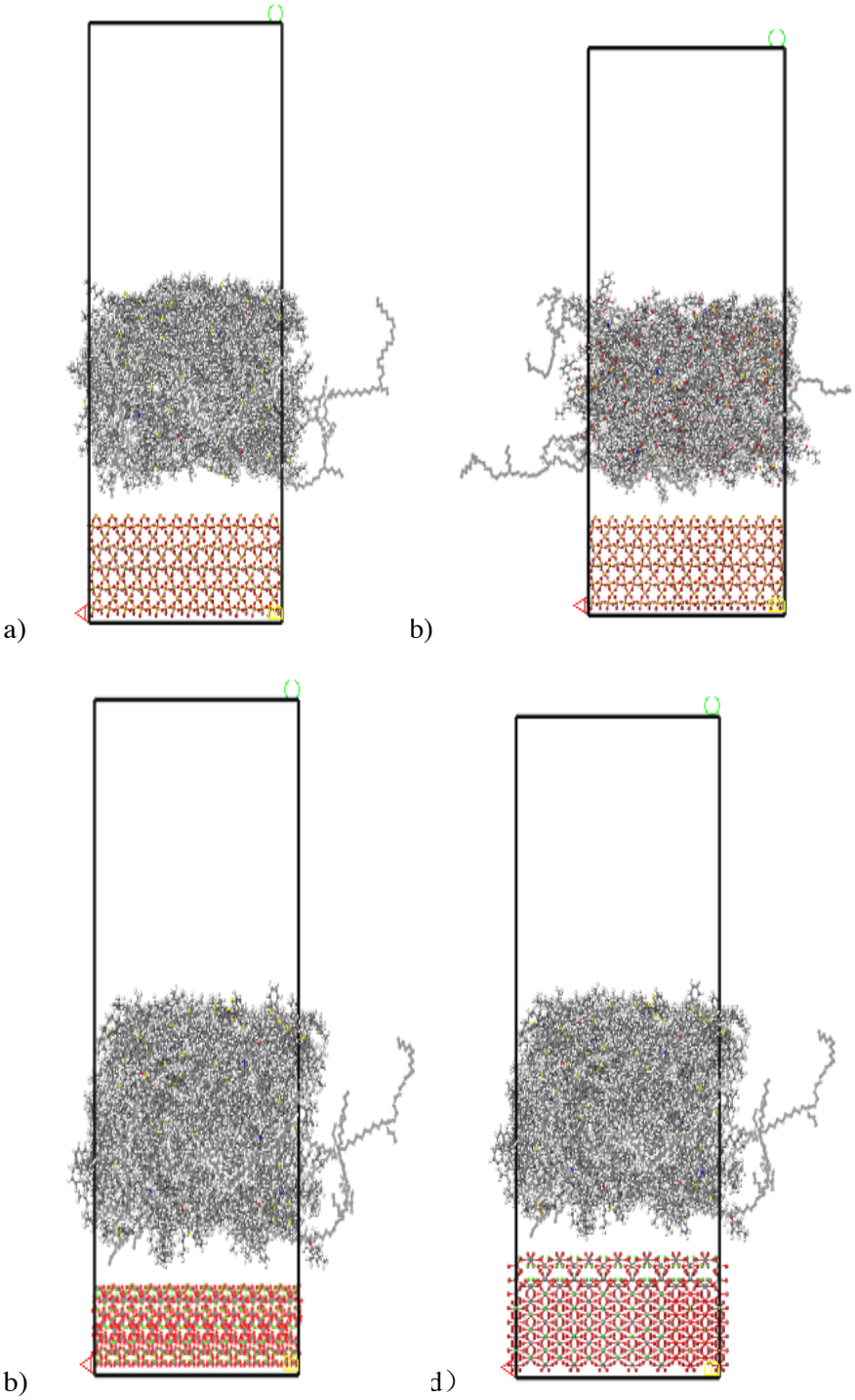


Figure 3.12 the LDPE modified virgin or LDPE modified oxidized bitumen-mineral interface systems (a) the LDPE modified virgin bitumen-quartz model, (b) the LDPE modified oxidized bitumen-quartz model, (c) the LDPE modified virgin bitumen-Calcite model, (d) the LDPE modified oxidized bitumen-calcite model.

3.4.3 LDPE modified virgin or oxidized bitumen-mineral interface systems - dry Process

As stated in the Chapter 2, the LDPE can be introduced into the asphalt using the dry process. In comparison with the wet process, the LDPE general are poured over the aggregate in order to form LDPE coated aggregate before adding bitumen (see Figure 3.13). Therefore, for reasonable model construction, a confined LDPE layer is attached to the mineral substrate forming the LDPE coated mineral layer. And then the LDPE coated mineral layer is attached to the bitumen layer.

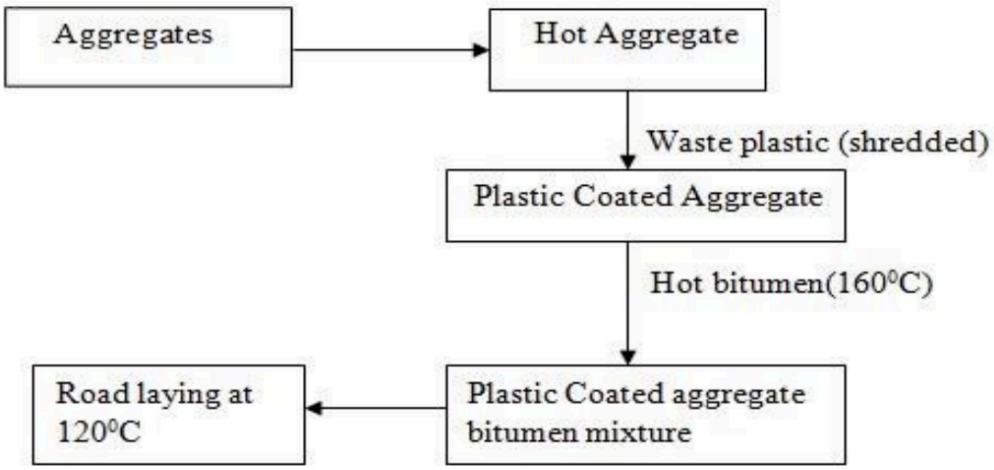


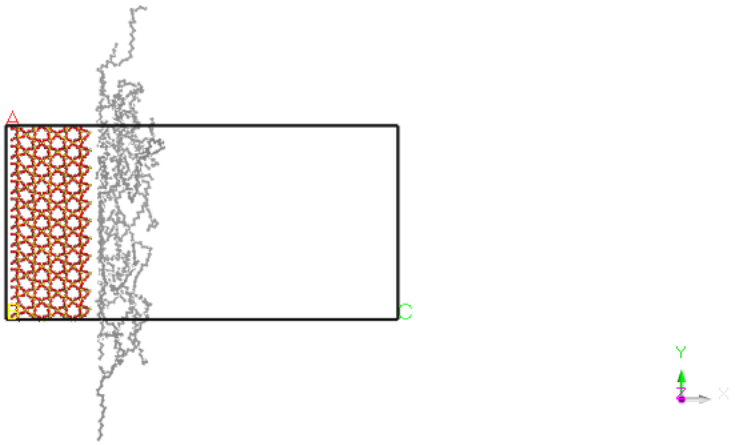
Figure 3.13 Flow chart of dry process (Nigam.S. et al, 2009).

3.4.3.1 LDPE - mineral interface (LDPE coated mineral).

In order to construct the LDPE-mineral interface system models, a thin confined layer with 10 molecules of LDPE is constructed with thickness of 15Å. The number of LDPE molecules

is determined by about 18% mass of bitumen. Also, the LDPE confined layer is also built with the similar surface area as the confined layer of mineral. Finally, a vacuum slab with 70Å is placed over the top surface of the LDPE layer. Once the LDPE coated mineral models are built, the models are subjected to the geometry optimization. After that, the interface systems are subjected to dynamic equilibration with NVT ensemble for 200ps with 1.0fs under the 298k temperature. Figure3.14 shows the interface systems for LDPE with two minerals at stable state.

a)



b)

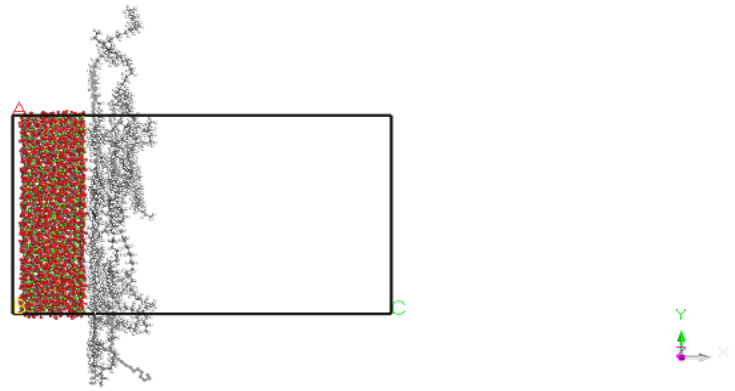
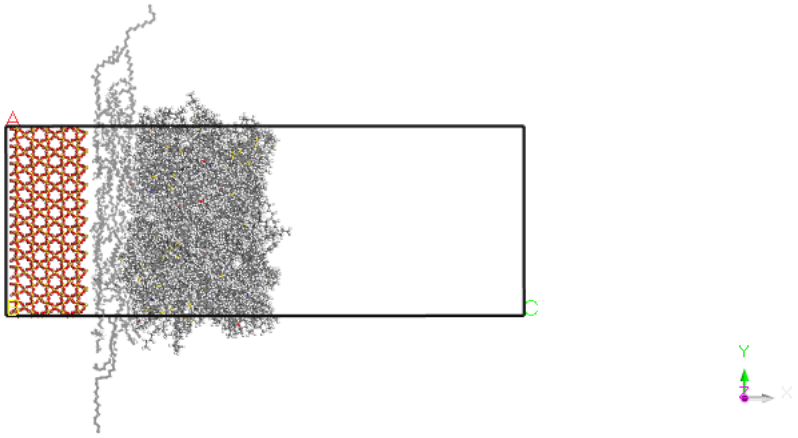


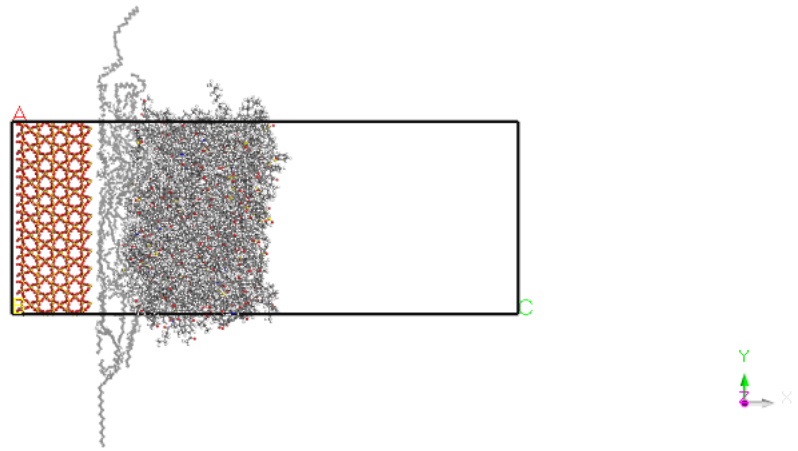
Figure 3.14. Interface systems between LDPE and minerals. (a). LDPE- quartz model. (b) LDPE-Calcite model.

3.4.3.2 Bitumen – LDPE coated mineral interface

Once the developed LDPE-mineral interface has been constructed, the bitumen-LDPE coated mineral interface system models can be built. Firstly, the virgin bitumen or oxidized bitumen layer is built with the similar surface to the layer of LDPE coated mineral. And then, the unmodified virgin or unmodified oxidized bitumen layer is optimized by using the geometry optimization and then followed by an NVT equilibration for 200ps. Thereafter, the developed virgin or bitumen layer is combined with the LDPE coated mineral model. A vacuum layer with thickness of 70Å was also attached on the top of the layer of bitumen. And the new models are built with the same procedures as the unmodified bitumen-mineral systems (see section 3.4.2). Figure 3.15 illustrates the four different bitumen-LDPE-mineral models.

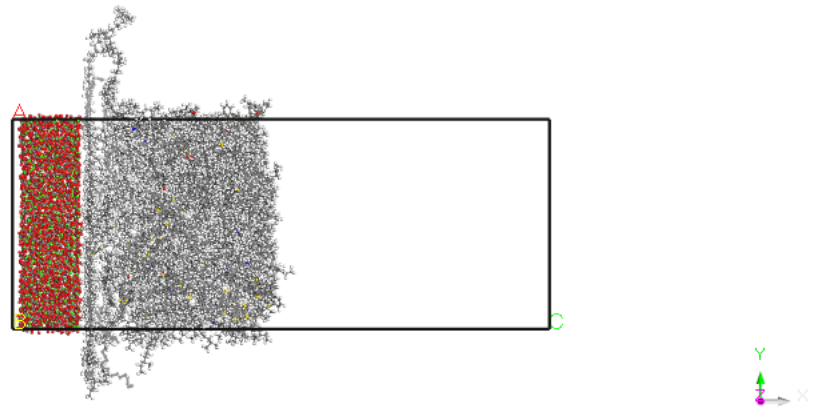


a)



b)

c)



d)

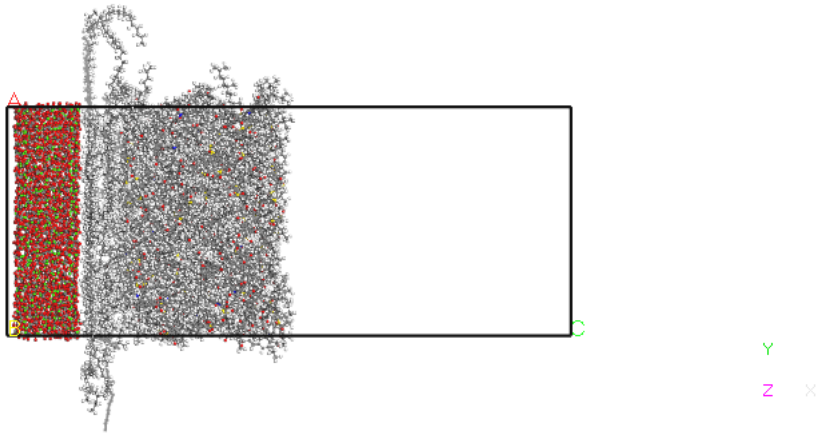


Figure 3.15 Interface system between bitumen and LDPE coated mineral. (a). virgin Bitumen- LDPE-Quartz. (b) Oxidized bitumen-LDPE-Quartz. (c) virgin bitumen-LDPE-Calcite. (d). Oxidized bitumen-LDPE-Calcite.

3.5 Methodology Summary

To summary, this chapter has discussed the research methodology undertaken by the researcher so that these can be used to achieve the aims of this study. In this chapter, the theory of molecular dynamic (MD) simulation has been explored. Secondly, the key parameters and formulas are also analyzed. Finally, all models built by the MD simulation which used in this research are also demonstrated.

Chapter 4 Data Analysis and Discussion

This chapter is discussed the results from the molecular dynamic (MD) simulations. This chapter is divided into the following parts:

1. Cohesive energy density within the bitumen & LDPE modified bitumen
2. Work of adhesion between the bitumen and minerals

4.1 Cohesive Energy Density (CED)

In MD simulations, the cohesive energy density can be defined as the increase in energy once all intermolecular forces are eliminated. As stated in the Chapter 2, the cohesion plays a vital role in the asphalt binder as it can affect the adhesive bond energy between the bitumen and minerals. Therefore, in this study, the cohesive energy density (CED) is used to measure the cohesive energy per unit volume in order to under understand the intermolecular force between atoms inside a bitumen molecule model. When calculating the CED value for a bitumen model, it is important that non-bond interaction within the bitumen has been taken account. Normally, the intermolecular interaction within the bitumen bulk include the van der Waals and electrostatic components.

4.1.1 Effect of oxidative ageing on cohesive energy density

The CED results for the virgin and oxidized bitumen are shown in the **Figure 4.1**

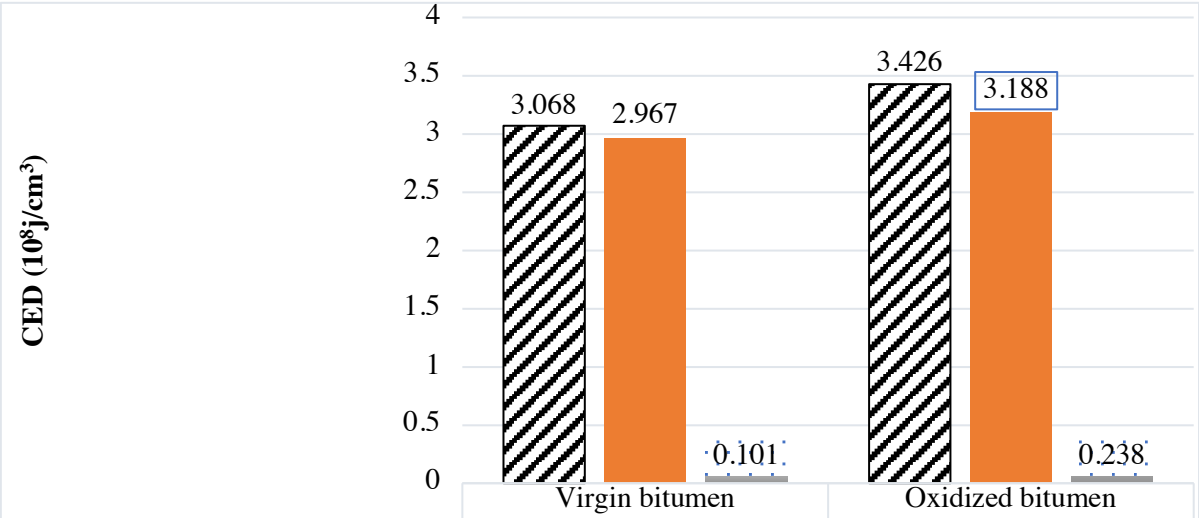


Figure 4.1 Cohesive energy density (CED) of virgin and oxidized bitumen (Total cohesive energy density= van der Waals energy + Electrostatic energy)

In this simulation, it is seen that the value of cohesive energy density (CED) increase with the aging (simulated by adding oxygen atoms into the virgin bitumen). For example, the calculated CED value for the virgin bitumen is the 3.068 x 10^8 j/cm^3. However, when the additional oxygen atoms are introduced into the virgin bitumen system, the CED value reaches to the 3.426 x 10^8 J/cm^3. The results tie well with previous studies. Mac Green (2012) indicated that the intermolecular bonding in the bitumen would increase when the oxygen atoms are introduced into the bitumen. The results also show that the CED is attributed to the non-bond interaction which consists of van der Waals interaction and electrostatic interaction. The main reason is the additional oxygen atoms can increase the both molecular weight and polarity of oxidized is much higher than the virgin bitumen. The van der Waals interaction is primary element of the intermolecular bonding in the bitumen. Moreover, from

previous studies, the oxygen atom is the more electronegative atoms as the bonds are polar so it also can also increase the polarity, which results in a higher electrostatic intermolecular interaction in bitumen model (Gao et al ,2018).

4.1.2 Combined effects of oxidative aging and LDPE on cohesion energy density.

Literatures stated the LDPE can be mixed into the virgin bitumen directly using the wet process. Therefore, this study helps to understand if the LDPE can affect the CED value in the bitumen at different aging state by using wet process. As previous explanation, the CED value increases with the increasing oxidation aging level, resulting in the stronger cohesive energy of oxidized bitumen compared to the virgin bitumen. The Figure 4.2 shows the calculated CED values for different bitumen models.

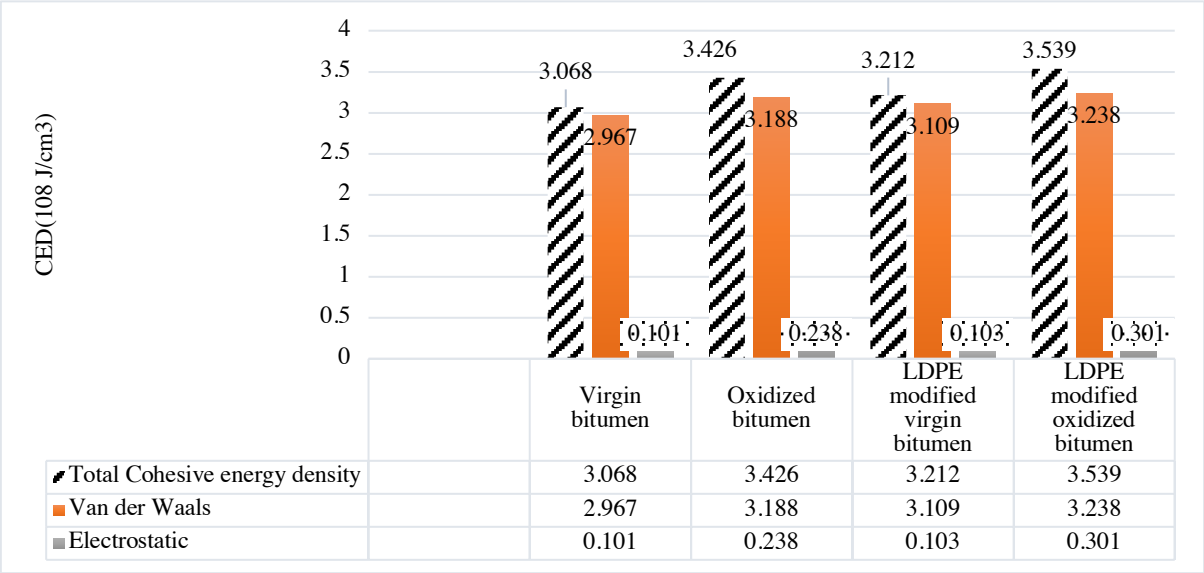


Figure 4.2 Cohesive energy density (CED) of virgin bitumen, oxidized bitumen, LDPE modified bitumen and oxidized LDPE modified bitumen (Total cohesive energy density= van der Waals energy + Electrostatic energy)

It is seen that the increase in LDPE content (by 9% weight) of asphalt binder led to an increase in cohesive energy density of the system. This is because CED value for virgin bitumen without aging is 3.068 x 10^8 J/cm^3, while the CED value for LDPE modified virgin bitumen is 3.212 x 10^8 j/cm^3. Additionally, the CED value for unmodified oxidized bitumen is 3.246 x 10^8 j/cm^3 and the value of CED for LDPE modified oxidized bitumen is 3.529 x 10^8 j/cm^3. Therefore, the results can be explained by the increase in intermolecular interactions due to the presence of LDPE molecules (9% weight). This is because the addition of LDPE molecules in the bitumen can lead to the higher portion of densely bitumen models. The LDPE molecules are non-polar molecules so it can only improve the molecular weight of bitumen model so that the van der Waals energy is increased after adding the LDPE molecules. However, Figure 4.2 also illustrates the electrostatic energy is also increased by a small amount after adding the five LDPE molecules. This is due to that, when the LDPE molecules applied into the oxidized bitumen model or virgin bitumen model, the distance between the molecules within the bitumen is getting closer. According to Eq (4), a smaller distance between the two molecules or atoms can increase the electrostatic energy. For example, if the distance between two heteroatoms is decrease, it can increase the polar bond energy between two heteroatoms so that it leads to increase in the electrostatic energy within the bitumen.

Therefore, these results obtained by adding the LDPE molecules and increasing oxygen content are both in a good agreement with the stiffening effect of bitumen mixture as the increased CED level, which means there is a stronger link between molecules after aging or

mixing with LDPE molecules. This result shows the server agglomeration of the bitumen could be caused when both adding the LDPE molecules and oxygen atoms into the virgin bitumen.

4.2. Work of Adhesion between Bitumen and Minerals

According to the Eq (1) and Eq (2), the total adhesive energy between the mineral and bitumen equals to the summation of non-bond energy and valance energy. However, in this study, the results indicate that the total adhesive energy equals to the non-bond energy including the van der Waals and electrostatic energy. This finding is also reported by the Gao et al (2008)'s study. Therefore, the total interfacial adhesion is purely resulted from the both van der Waals and electrostatic energy. In order to analysis if the different types of mineral can affect the adhesive energy between the mineral and bitumen, this section is divided into two parts, which are the work of adhesion for quartz-bitumen system and the work of adhesion for calcite-bitumen system, respectively.

4.2.1 Bitumen-Quartz adhesion

- Effect of oxidative aging on bitumen-quartz interface adhesion

To analysis the adhesion performance between the surface of quartz and surface of bitumen, the MD simulations have been used to calculate the work of adhesion for the quartz-bitumen interfacial system. The Figure 4.3 shows the work of adhesion for different bitumen-quartz interface models.

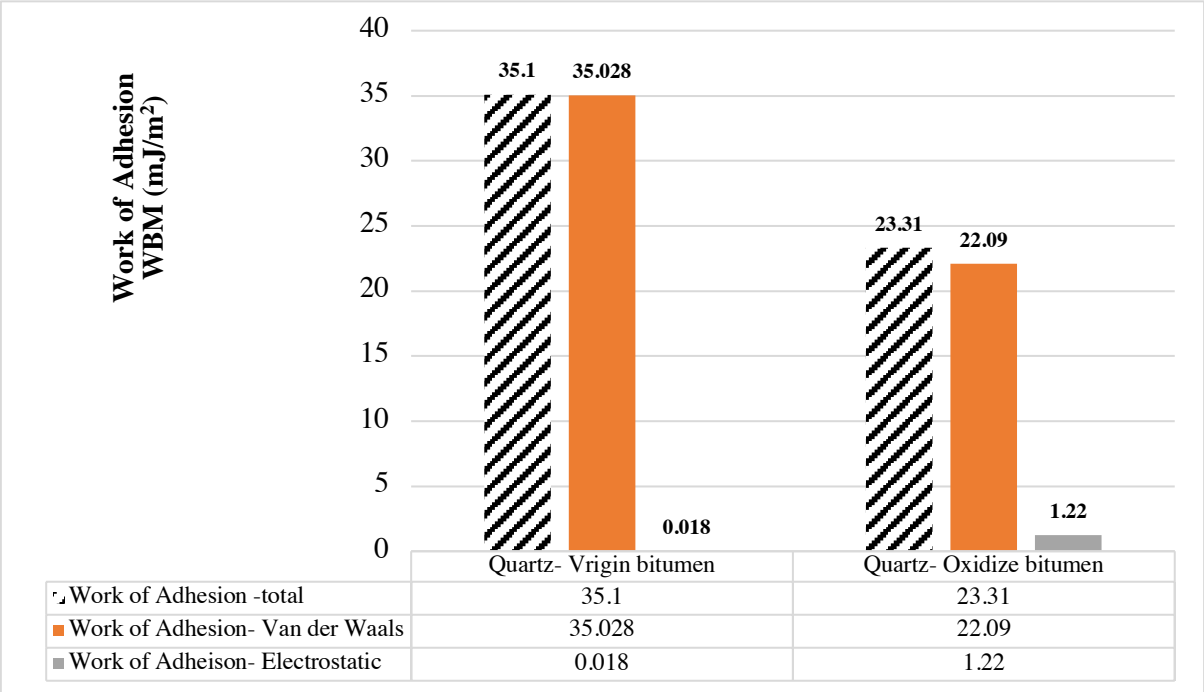


Figure 4.3 Work of adhesion for bitumen-quartz at different aging states (Non-bonded energy= adhesive energy= Van der Waals energy+ electrostatic energy.)

The Figure 4.3 illustrates that the oxidation level has a significant effect on adhesion performance between bitumen and quartz. This finding is consistent with that of Yi et al (2012) who found that the incorporation of extra oxygen atoms into the bitumen can weaken the bonding performance between the quartz and bitumen. Bitumen and quartz interact with each other mainly by van der wails energy, while the electrostatic energy plays negligible.

According to previous literature, the different types of mineral have different electric properties. Compare to the calcite-bitumen interface, the quartz is an electrically natural mineral so there is a weak electrostatic interaction between quartz and bitumen. The decreased work of adhesion is fundamentally caused by the decreased the van der Waals energy between bitumen and quartz when bitumen becomes aged. Therefore, the proportion

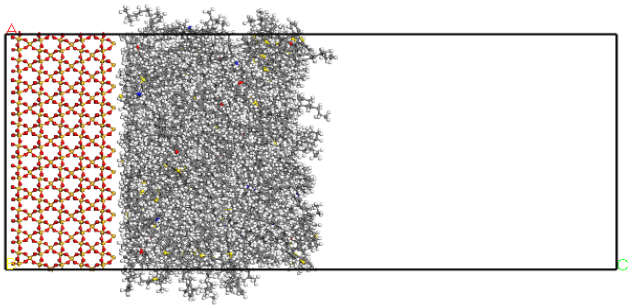
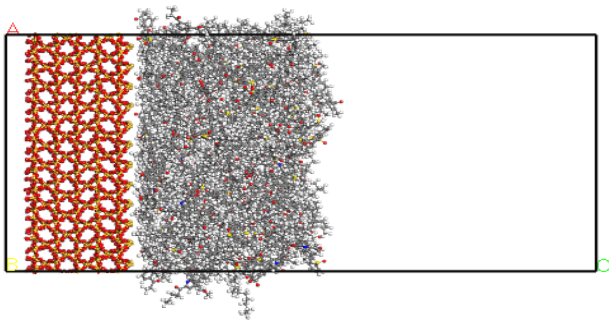
of resin and asphaltene fractions increased with the decreased proportion of aromatic and saturate. Therefore, as shown in the Figure 4.3, the work of adhesion between the virgin bitumen and quartz is 35.1mJ/m^2, which is much greater than the interface between the oxidized bitumen and quartz (23.31 mJ/m^2). According to the Eq (3), several studies presented that the center-to-center distance between the mass of bitumen and the mineral matrix can help to understand the variation for the bitumen-mineral models (Mizababaei 2017, Gao et al 2018). In this study, the center-to-center distance between the quartz matrix and bitumen mass is computed. As shown in the table 7, the center to center distance between the virgin bitumen and quartz is 41.14Å and 45.38Å for the oxidized bitumen-quartz system.

As stated in the last section, the bitumen becomes aged can cause server agglomeration of the bitumen molecules as compare to the virgin bitumen. This is because the additional oxygen atoms can enhance the cohesive energy density in the virgin bitumen. Therefore, the distance between the center of mass of the bitumen and matrix of quartz is getting bigger when the additional oxygen atoms are introduced into the virgin bitumen. As a result, based on the Eq (4), the greater distance between the bitumen and quartz can reduce the van der Waals energy between the surface of bitumen and the surface of the quartz and eventually weakens the work of adhesion between the bitumen and quartz. Figure 4.3 shows the electrostatic energy is increased slightly because more resin and asphaltene fractions are formed in the oxidized bitumen.

The van der Waals energy is the primary component of the interfacial adhesion between the bitumen and quartz. Although, the electrostatic energy is also increased after the aging

process, it still contributes little to the work of adhesion between the quartz and bitumen. Therefore, the work of adhesion of the bitumen-quartz model is decreased with the higher oxidation level.

Table 5. Center to center distance between bitumen mass and quartz matrix (1 Å = 1×10^{-10}m).

Interface models	Bitumen-Quartz	Center-to-center distance
Virgin bitumen-Quartz		41.14Å
Oxidized bitumen -Quartz		45.39Å

- **Effect of LDPE on bitumen-quartz interface adhesion**

To study the effect of Low-density polyethylene (LDPE) on the virgin bitumen-quartz adhesion, the model of LDPE modified bitumen -quartz interface and the model LDPE-

virgin bitumen-Quartz interface are used in the MD simulation in order to understand whether introducing LDPE into the bitumen can help improve the work of adhesion of bitumen-quartz system by using two mixing process, which are dry process and wet process, respectively.

(1) Effect of LDPE on bitumen-quartz interface adhesion (by Wet process)

In reviewing the literature, the LDPE could be introduced into the bitumen directly by using the wet process. Figure 4.4 shows the work of adhesion of the bitumen-quartz interface model with or without LDPE molecules.

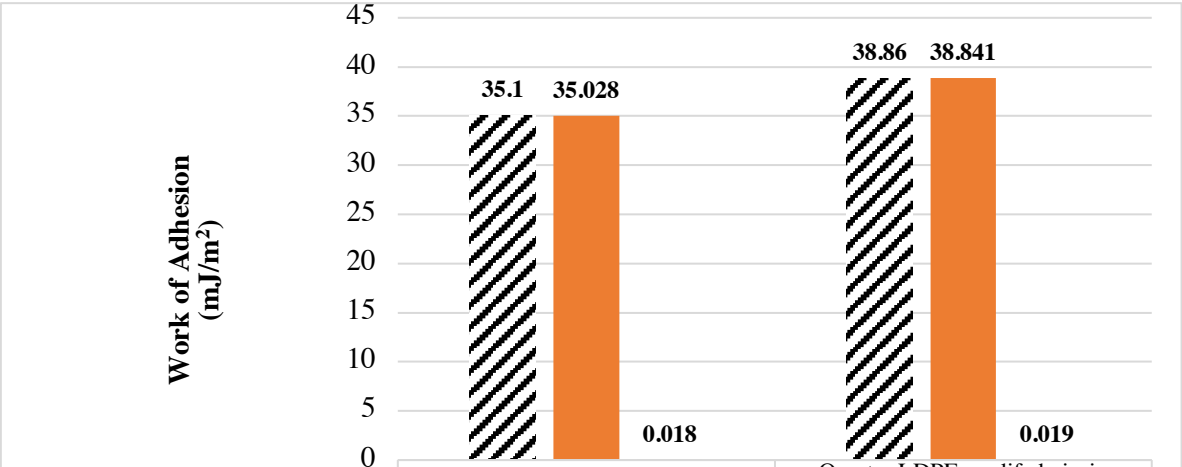


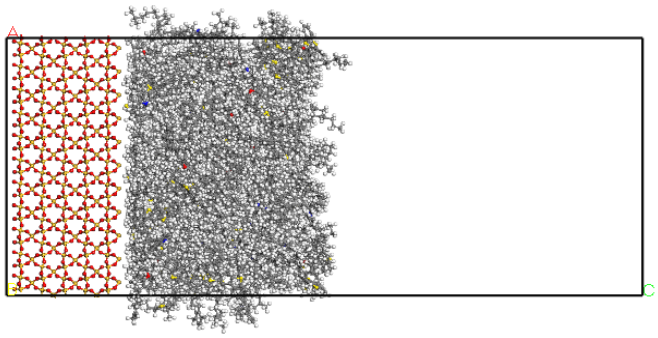
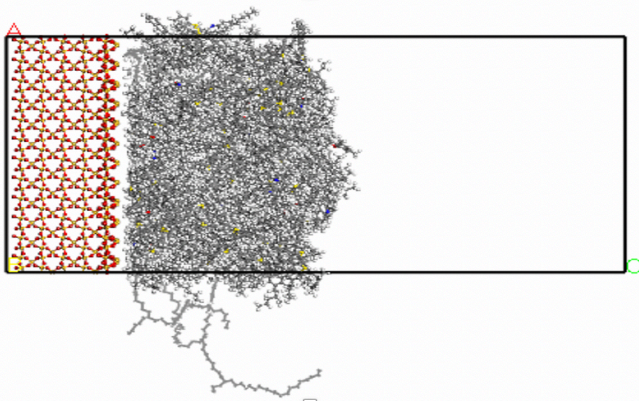
Figure 4.4 Work of adhesion of the bitumen-quartz model with or without LDPE molecules.

As stated in the chapter 3, there are 5 LDPE molecules are introduced into the virgin bitumen bulk model. Figure 4.4 shows the work of adhesion between the LDPE modified

bitumen and quartz is slightly higher than that of virgin model, Quartz is an acidic mineral having a strong van der Waals interaction with LDPE modified bitumen.

The increased the work of adhesion is caused by the increased van der Waals energy between the bitumen and quartz. Previous study has indicated the LDPE is a nonpolar molecule as it only consists of nonpolar and high molecular weight hydrocarbons, the chains of LDPE molecules are highly branches and results in much higher van der Waals energy. As a result, the van der Waals energy between quartz and bitumen is increased by adding the LDPE molecules and eventually improves the work of adhesion of bitumen-quartz model. LDPE molecule is purely compounded from carbon atoms and hydrogen atoms. Therefore, adding 5 LDPE molecules into the virgin bitumen cannot lead to form any polar functional groups so that the LDPE cannot cause a higher atomic charge in the bitumen. According to the Eq (3), the van der Waals energy is inversely proportional to the center -to- center distance, which means the higher van der Waals energy leads to a smaller distance between the bitumen mass and quartz matrix. Table 8 indicated the center -to- center distance is decreased from 41.14Å for the virgin bitumen-quartz model to the 37.16 Å for the LDPE modified virgin bitumen- quartz model.

Table 8 Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and quartz matrix (1 Å = 1×10^{-10}m).

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Quartz		**41.14** Å
LDPE modified virgin bitumen - Quartz		**37.16**Å

As state above, the quartz is an acidic mineral. For acidic mineral, Van der Waal is the major contributor for the adhesion between the bitumen and quartz. And the LDPE molecule is also a non-polar molecule so that it can only improve the work of adhesion by increase the van der Waals energy. In this case, the electrostatic interaction of acidic mineral with the acidic bitumen is weak. However, it can be found from Figure 4.4, the electrostatic energy is also increased with adding the LDPE molecules. This is because, the electrostatic energy is also inversely proportional to the distance between the two atoms. A smaller distance between the bitumen and quartz causes the stronger electrostatic interaction for the bitumen-quartz model, while if the bitumen is modified by the LDPE, the electrostatic energy is still not a key factor influencing the adhesion between bitumen and acidic mineral.

(2) Effect of Low-density polyethylene (LDPE) on bitumen-quartz interface adhesion (by Dry process)

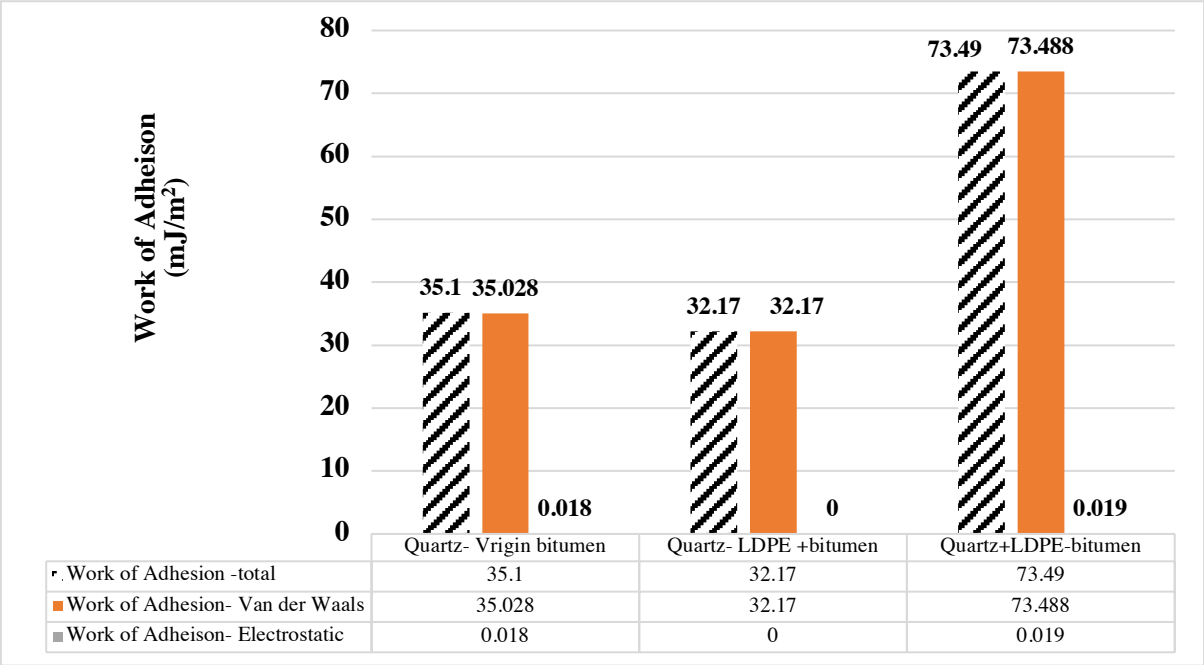
As stated in the last chapter, the 10 LDPE molecules (18wt%) is placed on the surface of quartz layer. This is because, in the dry process, the LDPE is usually coated on the surface of mineral before the mineral mixes with the bitumen. To understand the effect of LDPE on the work of adhesion between the quartz and virgin bitumen. The work of adhesion of quartz-LDPE-Bitumen model is calculated using the MD simulation and the results are compared with the work of adhesion for Quartz-Virgin bitumen model. In this study, the work of adhesion between the bitumen + LDPE and quartz and the work of adhesion between Quartz + LDPE and bitumen are both calculated because the interfacial adhesion between LDPE and quartz and the interfacial adhesion between LDPE and bitumen are two key factors influencing adhesion performance.

It can be seen from the Figure 4.5, the work of adhesion for the Quartz+LDPE-bitumen interface system is 79.448 mJ/m^2, which shows there is a significant improvement in comparison with the work of adhesion for quartz-virgin bitumen interface model. Figure 4.5 also indicates that the van der Waals plays a major part for Quartz+LDPE-bitumen interface systems, while the electrostatic energy is the negligible. This is fundamentally due to that the chemical formula of the LDPE molecule is $(C_2H_4)_n$, which only consists of carbon atoms and hydrogen atoms. Additionally, the thickness of LDPE layer is 15.16Å so that the quartz and bitumen would not interact with each other.

Figure 4.5 also shows the work of adhesion between the quartz and LDPE+ bitumen is 32.17mJ/m^2, which is lower than that of quartz-bitumen model. This is because the van der Waals energy for the Quartz-LDPE+bitumen is reduced compares to the van der Waals energy for virgin bitumen-quartz model. According to the Eq 4 and Eq 5, the electrostatic and van der Waals are both inversely proportional to the distance between two atoms. As shown in the Table 9, the center-to-center distance is 41.14Å for bitumen-quartz model, which is smaller than the distance between quartz- LDPE and bitumen (41.16 Å). Thus, it can be inferred that the distance between quartz and bitumen is getting bigger after adding LDPE molecules. In this case, the work of adhesion for the quartz-bitumen model could be reduced by adding the 10 LDPE molecules(18wt%). Therefore, the adhesion performance of the quartz-LDPE-Bitumen model could be determined by the Quartz-LDPE+bitumen interface system. Although, the interfacial adhesion energy decreased with the decrease of van der Waals energy and electrostatic force, the van de Waals energy still constitutes a major part in Quartz-LDPE-bitumen model, while electrostatic energy takes up a small proportion. As stated above, the bitumen and quartz cannot interact with each other because the thickness of layer of LDPE is more than15Å.This is reasonable that the van der Waals energy is the main factor determining adhesion performance between the Bitumen+ LDPE and quartz and it can be explained by the acid-base theory that quartz is acidic mineral and there are non-polar dipoles present in LDPE molecules.

Figure 4.5 also indicates the work of adhesion for the bitumen+ LDPE- quartz interface system and the work of adhesion for the Quartz+ LDPE-bitumen interface system. From Figure 4.5, the interfacial adhesion performance between the Quartz and LDPE+bitumen has a little

effect on the adhesion performance for the bitumen-LDPE- quartz model as there is a relatively weak bond energy between the quartz and LDPE. This is because the work of adhesion is reduced from 35.1mJ/m^2 for the virgin bitumen-quartz model to 32.17 mJ/m^2 for the Bitumen +LDPE-quartz model (see Figure 4.5). This result indicated that the incorporation the LDPE into asphalt binder by dry process cannot help to improve the adhesion performance of asphalt mixture.

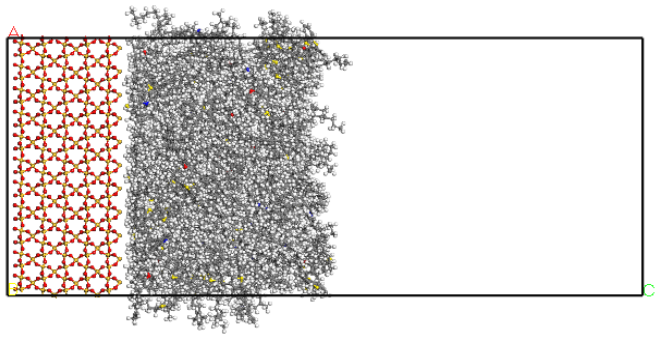
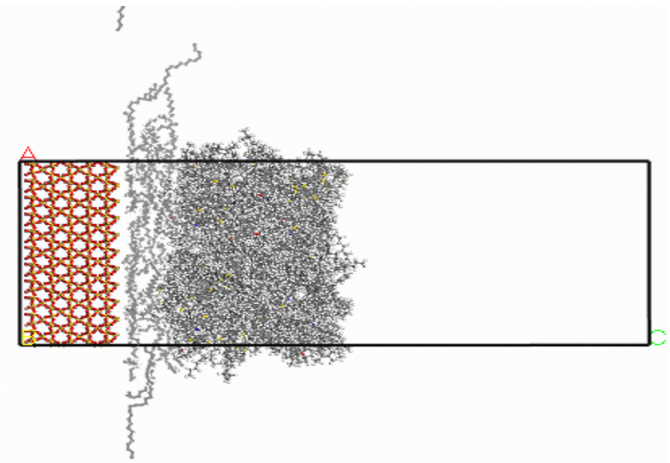


1

Figure 4.5 Work of adhesion of the bitumen-quartz model with or without LDPE molecules (dry process).

Table 9. Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and quartz matrix (1 Å = 1×10^{-10}m).

1

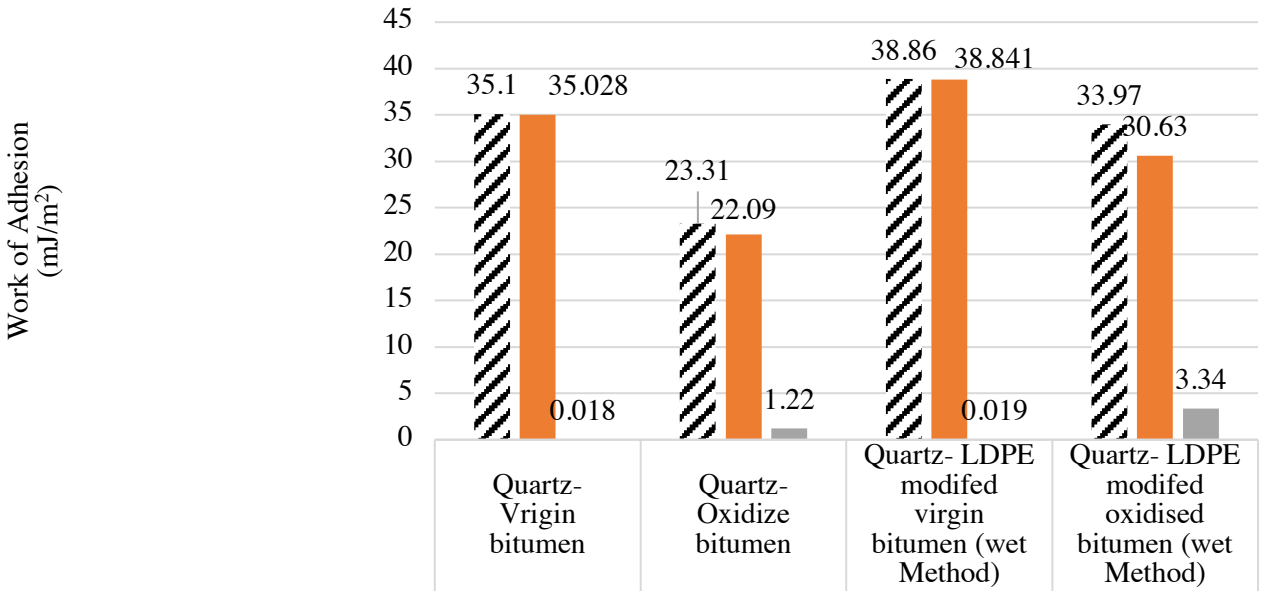
Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Quartz		**41.14** Å
Quartz+LDPE-Bitumen		**30.22** Å
Quartz-LDPE+Bitumen		**41.16** Å

As stated above, the incorporation of LDPE into the asphalt binder by wet process can improve the adhesion performance for quartz -bitumen model. In contrast, the presence of LDPE molecules (by dry method) could separate the bitumen from the quartz so that the adhesion performance of quartz-LDPE-bitumen interface model is determined by the adhesion interaction between the quartz and LDPE +bitumen because there is a relative weak van der Waals interaction between the quartz and LDPE, leading to the very weak adhesive energy between quartz and LDPE+ bitumen.

- **Combined effects of LDPE and oxidative aging on bitumen-quartz interface adhesion**

To clearly describe the combined effects of LDPE and oxidative aging on the bitumen-quartz interface adhesion, the LDPE molecules are introduced into the oxidized bitumen – quartz model by using two different mixing process.

(1) Combined Effects of LDPE and oxidative aging on bitumen-quartz interface adhesion (by Wet process).



	Quartz-Vrigin bitumen	Quartz-Oxidize bitumen	Quartz- LDPE modifed virgin bitumen (wet Method)	Quartz- LDPE modifed oxidised bitumen (wet Method)
Work of Adhesion -total	35.1	23.31	38.86	33.97
Work of Adhesion- Van der Waals	35.028	22.09	38.841	30.63
Work of Adheison- Electrostatic	0.018	1.22	0.019	3.34

Figure 4.6 Work of adhesion of the unmodified or modified bitumen-quartz models at different aging state (by Wet process).

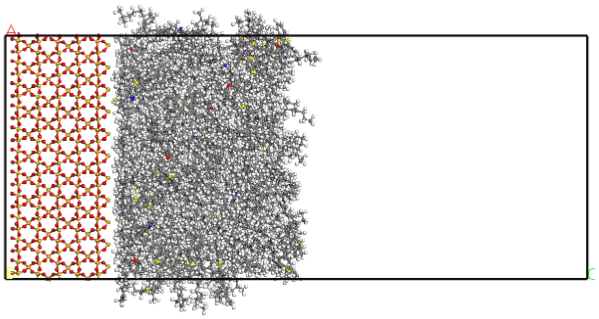
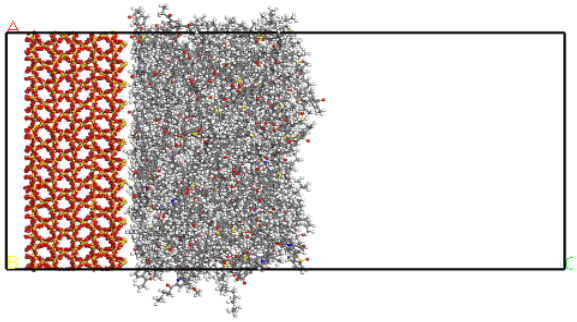
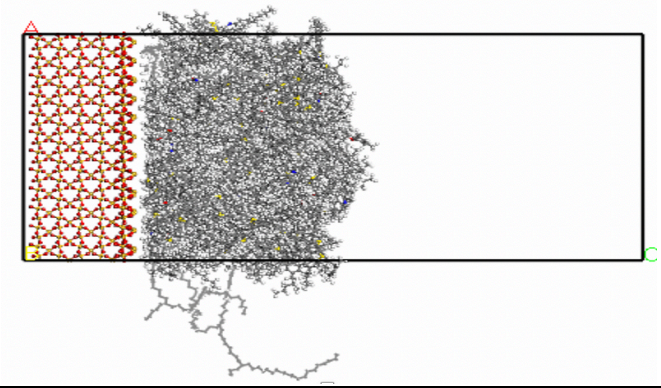
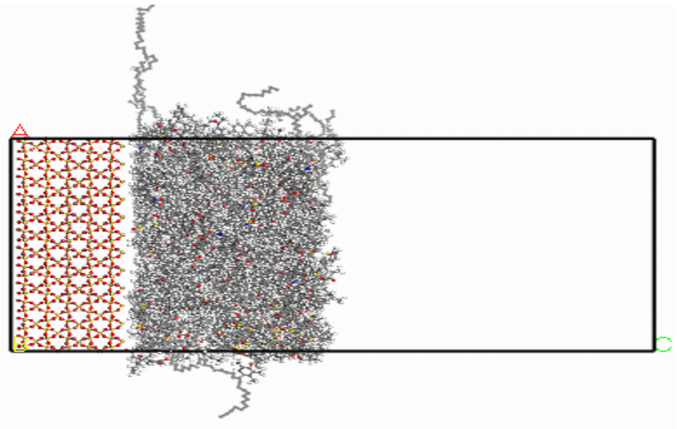
Figure 4.6 shows the work of adhesion of the bitumen-quartz interface models at different oxidation levels with or without LDPE. It can be seen from the Figure 4.6; the work of adhesion is reduced from 38.86mJ/m^2 for LDPE modified virgin bitumen -quartz interface model to 33.97mJ/m^2 for the LDPE modified oxidized bitumen interface model. Therefore, it was found that the work of adhesion between the LDPE modified bitumen and quartz decreased with the increase of oxidization level. The main reason is the van der Waals energy reduced with the increase of the oxidation level. This is due to, for the acidic mineral, van der Waals is the main contributor for adhesive energy between LDPE modified bitumen and quartz so that the decrease of van der Waals energy is caused by the increase of the distance between modified bitumen and quartz as shown in the Table 10. As stated above, the molecular weight of bitumen and cohesive energy density (CED) increased when the additional oxygen atoms applied into the virgin bitumen. Similarly, the higher oxidation level can cause a stronger aggregation of LDPE modified bitumen. Thus, it can be inferred that the higher value of CED can increase the distance between the LDPE modified bitumen and quartz and eventually weaken the work of adhesion between LDPE modified bitumen and quartz.

From Figure 4.5, The additional LDPE molecules in the oxidized bitumen model has a significant effect on the interfacial adhesion energy between the oxidized bitumen and quartz. This finding shows the work of adhesion for the oxidized bitumen- quartz model is 23.31 mJ/m^2. After adding 5 LDPE molecules into the bitumen, the work of adhesion for LDPE modified oxidized bitumen-quartz interface model is increased to 33.97 mJ/m^2. As

mentioned before, the LDPE molecule consists of nonpolar and high molecular weight hydrocarbons. Therefore, the additional five LDPE molecules in the oxidized bitumen has a positive effect on improving the adhesion energy between the oxidized bitumen and quartz with the increased van der Waals force between oxidized bitumen and quartz.

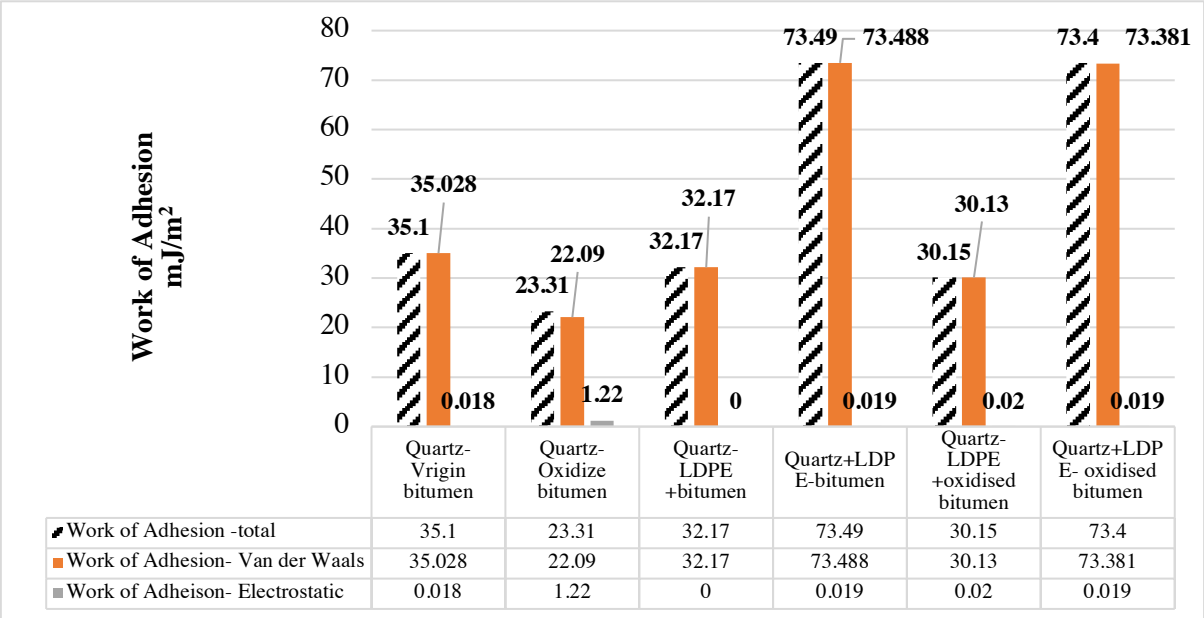
As observed above, the work of adhesion for the bitumen-quartz interface model decreased after aging process. However, as shown in the figure 4.5, the negative effect of oxidative aging on the bitumen-quartz model cannot be remedied by adding the LDPE molecules into the bitumen. It can be inferred that the oxidative aging has a very strong effect on the bitumen-quartz interfacial adhesion performance. This is because, the higher oxidation level can increase the distance between the quartz and bitumen due to the stronger aggregation of the bitumen after aging. According to the Eq (4), the van der Waals force is inversely proportional to the center-to-center distance between bitumen and quartz. Therefore, in this study, considering that the content of LDPE molecules (9wt%) in the oxidized bitumen is very low, which has a little effect on improving the van der Waals energy between the oxidized bitumen and quartz. This finding is unexpected and suggests that mixing the low-content of LDPE into asphalt binder cannot minimize the negative effect of oxidative aging on the bitumen-quartz interfacial adhesion performance.

Table 10 Center to center distance between LDPE modified or unmodified bitumen mass and quartz matrix at different aging state (1 Å = 1×10^{-10}m).

Interface models	Bitumen-Quartz	Center-to-center distance
Virgin bitumen-Quartz		**41.14**Å
Oxidized bitumen -Quartz		**45.39** Å
LDPE modified virgin bitumen -Quartz		**37.16** Å
LDPE modified oxidised bitumen -Quartz		**43.21** Å

(2) Combined effect of Low-density polyethylene (LDPE) and oxidative aging on bitumen-quartz interface adhesion (Dry process).

The LDPE effect on the bitumen-quartz interface system studied by adding 10 LDPE molecules (18wt%) into the quartz-bitumen interface model (by dry process). Therefore, as observed above, the adhesion performance for quartz-LDPE -bitumen model is determined by the interfacial adhesion between bitumen and LDPE+ quartz and interfacial adhesion between quartz and LDPE+bitumen. Therefore, the work of adhesion for the Quartz+LDPE-bitumen interface model and work of adhesion for Bitumen+ LDPE- quartz interface model are both calculated based on the MD simulation (see Figure 4.7).



	Quartz-Vrigin bitumen	Quartz-Oxidize bitumen	Quartz-LDPE +bitumen	Quartz+LDPE-bitumen	Quartz-LDPE +oxidised bitumen	Quartz+LDPE- oxidised bitumen
Work of Adhesion -total	35.1	23.31	32.17	73.49	30.15	73.4
Work of Adhesion- Van der Waals	35.028	22.09	32.17	73.488	30.13	73.381
Work of Adheison- Electrostatic	0.018	1.22	0	0.019	0.02	0.019

Figure 4.7 Work of adhesion of the bitumen-quartz model with or without LDPE molecules at different aging state (dry process).

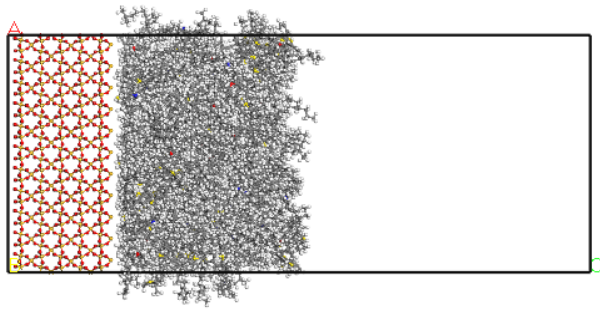
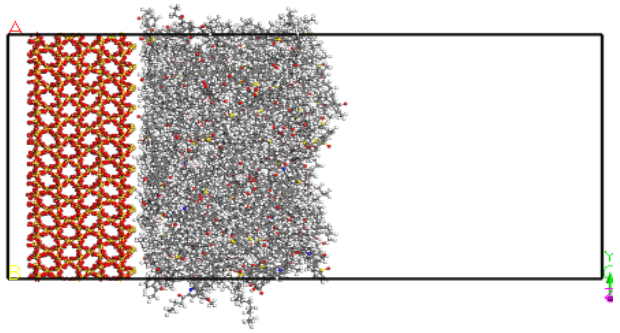
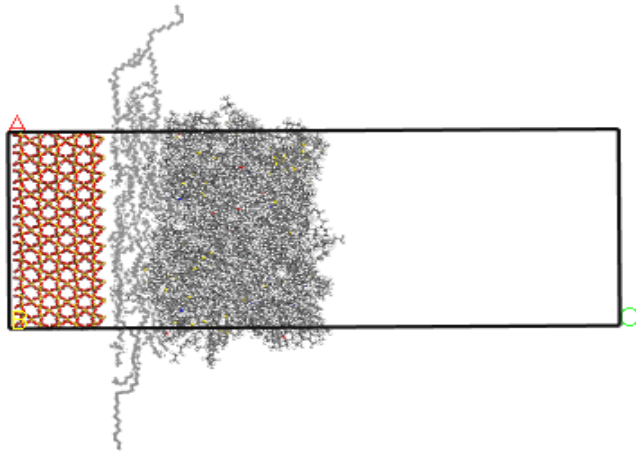
The quartz is the acidic mineral (neutral mineral) so that the van der Waals is the primary contributor for bitumen-quartz interface adhesion energy. As can be seen from the Figure 4.6, the oxidative aging and LDPE are two key factors could influence interfacial adhesion performance for Quartz-LDPE-bitumen interface model. To describe the combined effects of oxidative aging and LDPE on bitumen-quartz interface model, the work of adhesion between the oxidized bitumen and LDPE+ quartz and the work of adhesion between the quartz and LDPE+ oxidized bitumen is all analyzed.

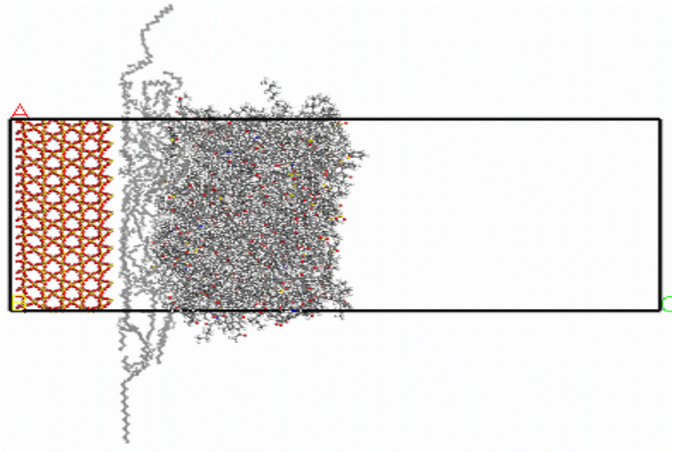
Figure 4.7 shows the work of adhesion is first increased from 35.1mJ/m^2 for virgin bitumen- quartz model to 73.49 mJ/m^2 for the quartz +LDPE-virgin bitumen model when the 10 LDPE molecules(18wt%) are introduced into the quartz-bitumen interface model (by dry method)and then the work of adhesion for the quartz +LDPE-virgin bitumen interface model is decreased slightly when the bitumen becomes aged. As shown in the Figure 4.7, the work of adhesion between quartz+LDPE -virgin bitumen is 73.49 mJ/m^2, while the work of adhesion between quartz+LDPE -oxidized bitumen is 73.4 mJ/m^2. These results indicated that the van der Waals interaction contributes the main adhesion between Quartz + LDPE-bitumen model. This is reasonable because the quartz is an electronically neutral mineral and there is no electrostatic bond exists in the interface between the LDPE and bitumen as the LDPE is non-polar molecule. Moreover, the results also indicated the LDPE has a positive effect on the interface adhesive energy between bitumen and quartz, while the oxidative aging could reduce the van der Waals energy, where van der Waals is the primary component of the adhesion between quartz and bitumen. Unlike the work of adhesion between the virgin

oxidized bitumen and quartz, the aging is not the key factor influencing interface adhesive energy between the Quartz+LDPE and oxidized bitumen

As observed above, the adhesion performance of the quartz-LDPE-Bitumen model is determined by the adhesion energy between the Quartz and LDPE+bitumen. Therefore, in this study, the work of adhesion for the oxidized Bitumen+ LDPE- quartz interface model is also calculated based on the MD simulations. As can be seen from the Figure 4.7, when the 10 LDPE molecules placed upon the quartz layer, the work of adhesion decreases from 35.1 mJ/m^2 for virgin bitumen-quartz model to 32.17 mJ/m^2 for Quartz-LDPE+virgin bitumen interface model, resulting from the lower van der Waal interaction between the quartz and LDPE (that reason is presented in the previous section). Once the additional oxygen atoms are introduced into the virgin bitumen, the work of adhesion is further decreased from 32.17 mJ/m^2 for bitumen+LDPE-Quartz model to 30.15 mJ/m^2 for oxidized bitumen +LDPE-Quartz model. The main reason is LDPE molecules is more likely to adhere to bitumen than quartz, so when the oxygen atoms are introduced into the bitumen it may cause a server agglomeration of the bitumen molecules, leading to a greater distance between the Bitumen+LDPE and quartz (see table 11). As a result, according to the Eq (4) and Eq (5), the electrostatic energy and van der Waals are both decreased between the LDPE and quartz with the greater distance between the quartz and LDPE.

Table 11. Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and quartz matrix at different aging state (1 Å = 1×10^{-10}m).

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Quartz		**41.14** Å
Oxidized bitumen - Quartz		**45.39** Å
Quartz+LDPE-Bitumen		**30.22** Å
Quartz-LDPE+Bitumen		**41.16** Å
Quartz +LDPE-oxidized bitumen		**33. 16** Å

Quartz- LDPE+oxidized bitumen		**43.28** Å

In conclusion, these results suggest that the oxidative aging and LDPE can both affect the adhesion performance between bitumen and quartz. The oxidative aging has a significant negative effect on the interfacial adhesion energy between bitumen and quartz. Comparing the work of adhesion for quartz -LDPE+ virgin bitumen interface model and work of adhesion for quartz -LDPE+ oxidized bitumen, the addition of 10 LDPE molecules cannot enhance interfacial adhesion energy between the quartz and LDPE + bitumen ,which may be related to the low content of LDPE in the model.

4.2.2 Bitumen-Calcite adhesion

- Effect of oxidative aging on bitumen-Calcite interface adhesion

The clearly understand the interfacial adhesion performance between the bitumen (at different oxidation degree) and calcite (alkaline mineral), the work of adhesion for different bitumen-calcite systems are calculated according to the MD simulation results. The work of adhesion for these different interface models are shown in Figure 4.8.

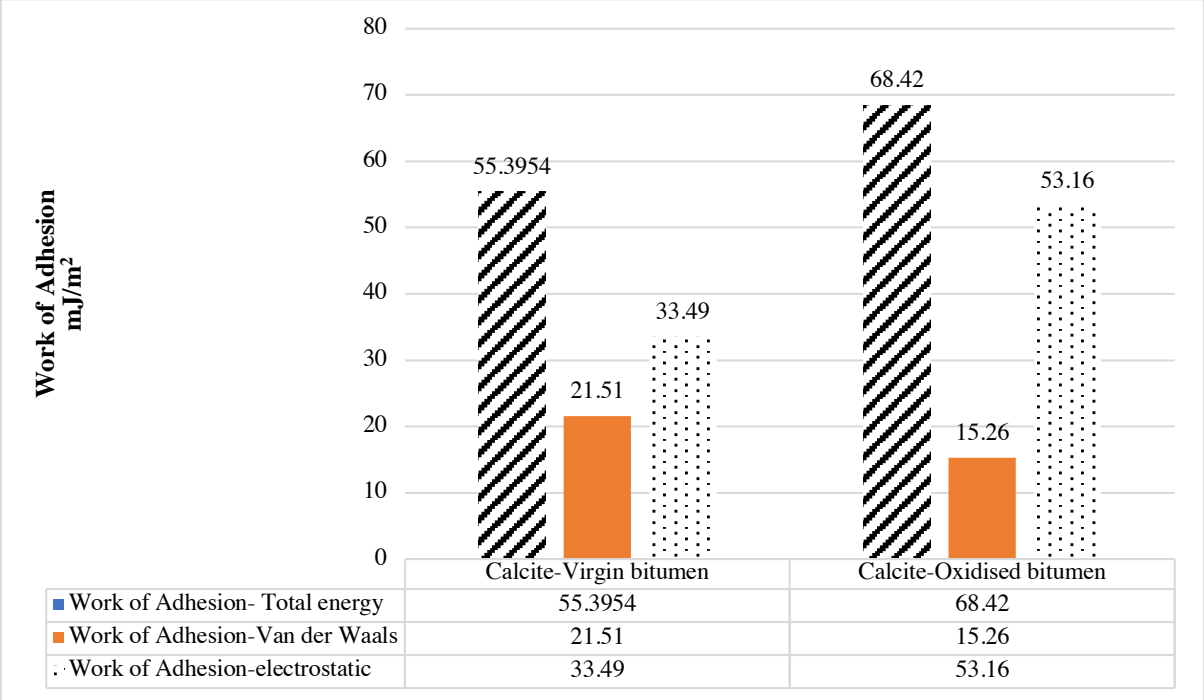


Figure 4.8 ***Work of adhesion for bitumen-Calcite at different aging states (Non-bonded energy= adhesive energy= Van der Waals energy+ electrostatic energy.)***

Figure 4.8 shows the work of adhesion for virgin bitumen-calcite and oxidized bitumen-calcite interface models. Unlike the work of adhesion between bitumen and quartz, the Figure 4.8 indicates the work of adhesion increased from 55.39mJ/m^2 for the calcite- virgin bitumen interface model to 68.42 mJ/m^2 for oxidized bitumen-calcite interface model. The change is mainly resulted from the increase of electrostatic energy. In the calcite-bitumen interface model, the electrostatic energy constitutes a major part, while the van der Waals only takes up a small proportion. According to the acid base theory, the bitumen is an acidic material and more likely adheres to alkaline minerals (e.g. calcite) with a strong strength（Gong et al 2017）. Therefore, the calcite is a weak alkaline mineral and the bitumen is acidic material so that bitumen has a strong adhesive energy with calcite (alkaline mineral). This finding is

also consistent with the previous study shows that the aggregate contains many alkaline minerals have a strong electrostatic adhesive energy with bitumen (Aguiar-Moya et al ,2015).

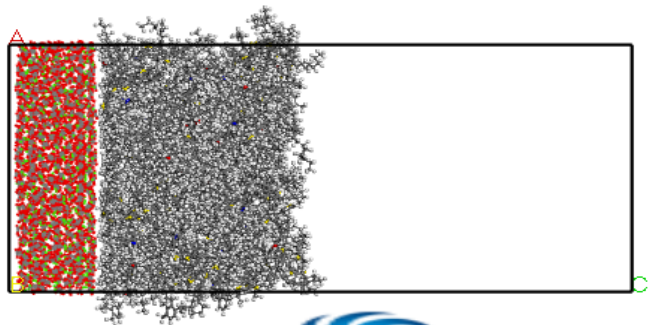
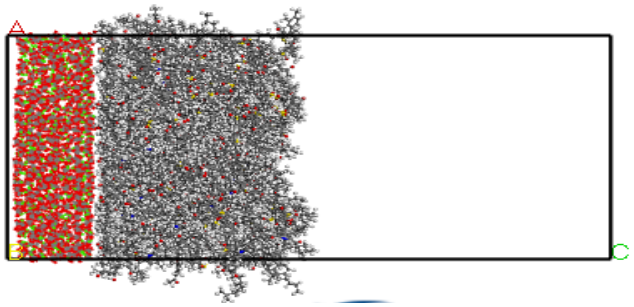
The Figure 4.8 also indicates that the electrostatic energy is increased with the after age. As mentioned in last section, the CED value is increased when the bitumen becomes aged so that the intermolecular force is improved within the bitumen. Therefore, when the bitumen becomes aged, the distance between the mass of bitumen and matrix of calcite is increased due to aggregation of bitumen molecules. According to the Eq (5), the greater distance due to the more aggregation of bitumen molecules can cause the lower electrostatic energy (see Table 12). However, the atomic charge is also one of the main factors influencing the electrostatic energy in an interfacial system. As a result, when the additional oxygen atoms are introduced into the bitumen, the atomic charge (electrostatic energy) is increased due to higher polarity.

Figure 4.8 shows the van der Waals energy decreased when the bitumen becomes aged. The decreased van der Waals is caused by the increased of the distance between the mass of bitumen and calcite matrix (see Table 12). However, unlike the adhesion energy between bitumen and quartz, the van der Waals has a little effect on the adhesion performance between the calcite and bitumen. Therefore, the change of van der Waals with the increase of the oxidization level is no longer the key factor affecting adhesion performance.

As motioned above, the electrostatic energy plays the major role in the interfacial system between the calcite and bitumen. Therefore, the electrostatic interaction is more helpful than van de Waals interaction to increase the interfacial adhesion energy between the

bitumen and calcite. Therefore, the work of adhesion for the calcite-bitumen interface model is increased after the aging process.

Table 12. Center to center distance between Bitumen mass and Calcite matrix at different aging state (1 Å = 1×10^{-10}m).

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Calcite		**43.04** Å
Oxidized bitumen - Calcite		**46.39**Å

- **Effect of LDPE on Bitumen-Calcite interface adhesion**

As stated in the section 3, there are two different mixing process can be used to mix the LDPE with the asphalt binder. According to the previous findings from bitumen -quartz interface systems, different mixing process can cause different effects on the interfacial adhesion performance for bitumen-mineral interface model. Therefore, in order to evaluate the effect of LDPE on the interfacial adhesion performance between the bitumen and calcite, the LDPE

molecules are introduced into the bitumen-calcite interface models using the two different mixing methods.

(1) Effect of LDPE on bitumen-Calcite interface adhesion (by Wet process)

To understand the effect of LDPE on interfacial adhesion performance between the LDPE modified bitumen and calcite, the five LDPE molecules (9wt%) are mixed into the bitumen directly using the wet process. The Figure 4.9 shows the work of adhesion for the LDPE modified bitumen-calcite model and virgin bitumen-calcite model.

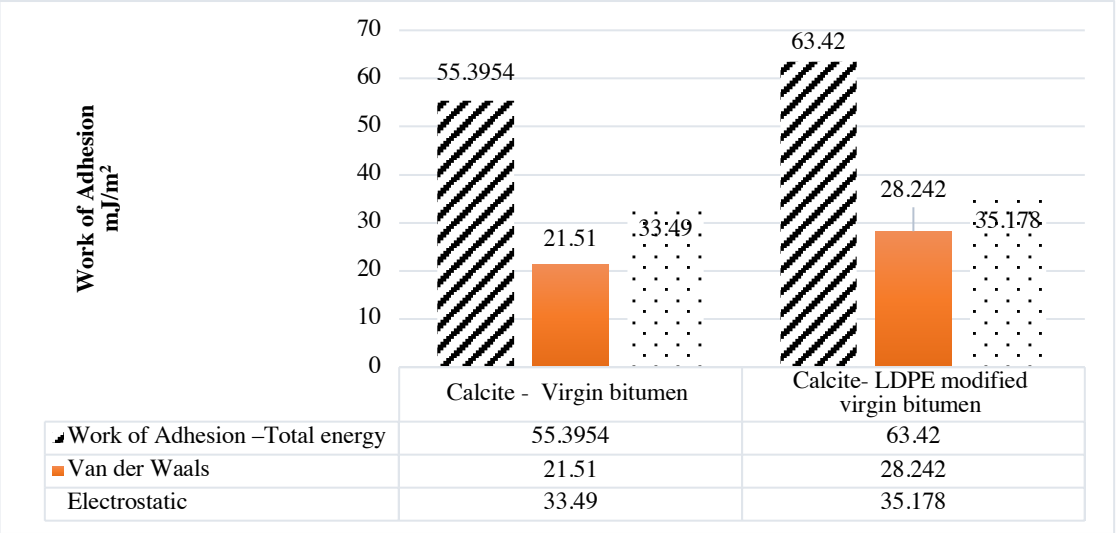


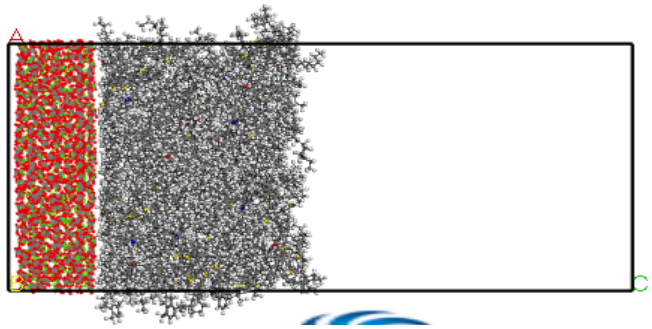
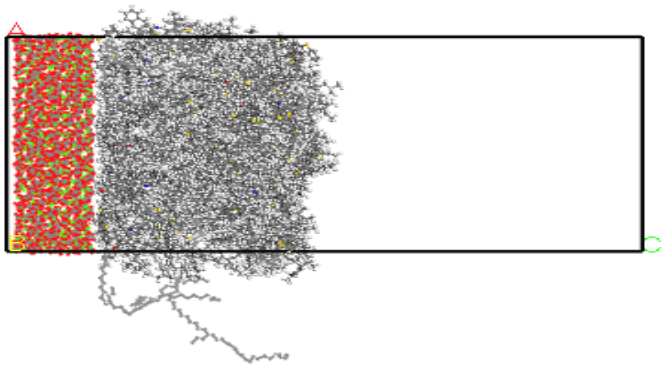
Figure 4.9 Work of adhesion of the bitumen-calcite model with or without LDPE molecules (by Wet process).

Figure 4.9 shows the LDPE molecules can help to improve the interfacial adhesion performance between the calcite and bitumen. The work of adhesion increases from 55.40mJ/m^2 for virgin bitumen-calcite interface model to 63.42mJ/m^2 for LDPE modified bitumen-calcite interface model. The positive effect of LDPE is due to the increased van der

Waals energy and the increased electrostatic energy. Firstly, the increased van der Waals energy is caused by introducing the five LDPE molecules (9wt%) into the virgin bitumen. As stated above, the LDPE is a nonpolar hydrocarbon molecule so that the high content of LDPE molecules in the bitumen results the higher van der Waals energy between the bitumen and calcite and eventually results a higher interfacial adhesive energy between the bitumen and calcite. Secondly, the increased electrostatic energy is caused by the decreased distance between the bitumen and calcite. The main reason is the van der Waals energy is inversely proportional to the distance between atoms according to the Eq (4). Therefore, the higher van der Waals can result a smaller distance between the bitumen and calcite. Based on the Eq (5), the distance between two molecules or atoms are also inversely proportional to the electrostatic energy so the smaller distance between the mass of bitumen and calcite matrix can result the higher electrostatic energy.

Although, the smaller center-to-center distance between the bitumen and calcite results from the increase of van der Waals energy (due to the introduction of 5 LDPE molecules). Figure 4.9 indicates that electrostatic component is a key factor affecting adhesion performance and interaction between LDPE modified bitumen and calcite. This because, the aggregate which contains lots of calcite has a strong electrostatic adhesion with bitumen.

Table 13. Center to center distance between LDPE modified Bitumen mass or mass of virgin bitumen and Calcite matrix (1 Å = 1×10^{-10}m).

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Calcite		**43.04**Å
LDPE modifed bitumen - Calcite		**42.09**Å

(2) Effect of the LDPE on bitumen-Calcite interface adhesion (by Dry process)

As stated above, the work of adhesion for mineral- LDPE- bitumen interface model is always smaller than that work of adhesion for the mineral -bitumen interface model and the interfacial adhesion performance between the bitumen and mineral can be affected when the LDPE is introduced into the asphalt binder using dry process. This is because, compared to the bitumen-LDPE+ Mineral interface, the interfacial adhesion energy between the Bitumen +LDPE and mineral is relatively low. In order to study the interfacial adhesion performance for the bitumen- LDPE-Calcite interface model, 10 LDPE molecules is placed between the calcite and bitumen layers. As shown in the Figure 4.10, the interfacial adhesive energy

between Bitumen+LDPE and calcite are relatively low in comparison with the adhesive energy between the Calcite+LDPE and bitumen. Firstly, as mentioned above, the adhesive energy performance can be determined by the adhesive energy between the calcite and LDPE+bitumen. Therefore, as shown in the Figure 4.10, the work of adhesion is reduced from the 55.40mJ/m^2 for the virgin bitumen-calcite model to 43.77 mJ/m^2 for the calcite-LDPE + bitumen model. This is because of the decrease of the electrostatic energy and decrease of the van der Waals energy. Firstly, the decreased electrostatic energy between the calcite and LDPE+bitumen is fundamentally caused by the increased the distance between the calcite and LDPE+ bitumen based on the Eq (5). The main reason is the LDPE have a better interfacial adhesion performance between the 10 LDPE molecules and the bitumen (70.71mJ/m^2). As a result, as shown in the Table 14, the smaller distance between the Calcite +LDPE and bitumen leads to the greater distance between the bitumen + LDPE and calcite. According to Eq (4), the van der Waals is also inversely proportional to the distance between two atoms the greater distance between the calcite and LDPE+ bitumen leads to the smaller van der Waals energy between the calcite and LDPE+ bitumen.

The interfacial adhesion for bitumen-weak alkali mineral (calcite) interfacial model is dominated by electrostatic energy interaction. Therefore, the interfacial adhesion performance between the calcite and LDPE+ bitumen is determined by the electrostatic interaction which can be reduced by the increase of the distance.

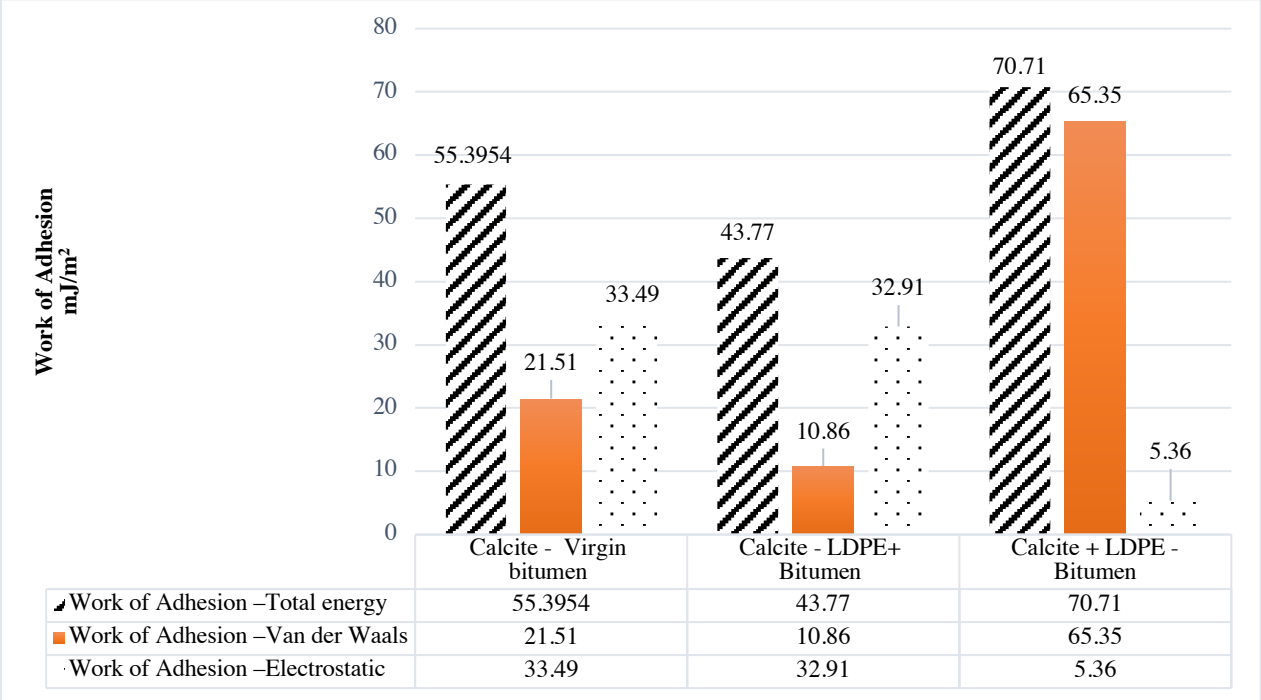
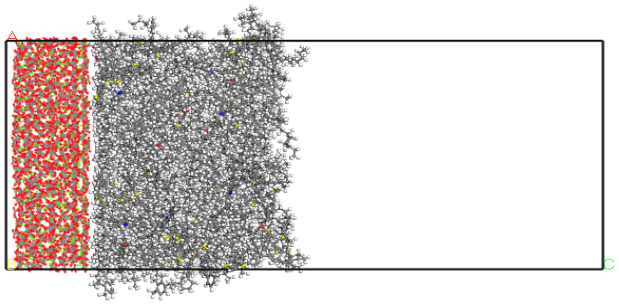
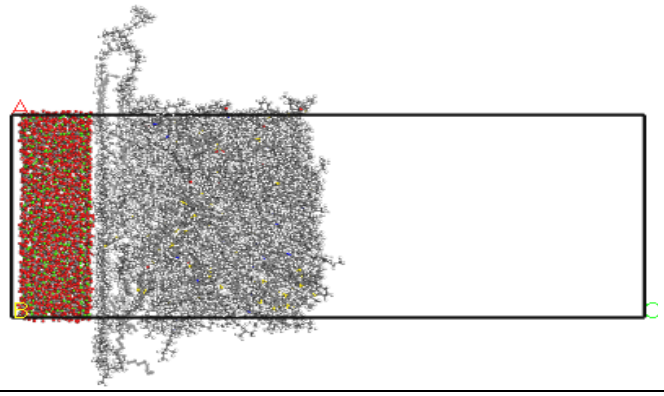


Figure 4.10 Work of adhesion of the bitumen-quartz model with or without LDPE molecules (by dry process).

Table 14. Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and Calcite matrix (1 Å = 1×10^{-10}m)- dry method.

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Calcite		**43.03** Å

Calcite +LDPE-Bitumen		**36.31** Å
Calcite-LDPE+Bitumen		**45.28** Å

- **Combined effects of the LDPE and oxidative aging on bitumen-Calcite interface adhesion.**

To clearly describe the combined effects of the aging and LDPE on the bitumen-calcite adhesion, the LDPE molecules are introduced into the oxidized bitumen bulk model by using two different mixing process.

(1) Combined effects of the Low-density polyethylene (LDPE) and oxidative aging on bitumen-Calcite interface adhesion (by wet process).

To understand the interfacial adhesion performance between the LDPE modified oxidized bitumen and calcite, the five LDPE molecules are introduced into the oxidized bitumen using wet process. Figure 4.11 shows the work of adhesion results for different bitumen-calcite interface models. Moya et al (2015) presented that the adhesive bond energy is increased for the bitumen-alkali mineral when the bitumen become aged. The electrostatic energy is primary contributor for non-bond energy between the calcite and bitumen. The additional oxygen atoms can cause server aggregation of bitumen, leading to increase the

distance between the bitumen and calcite. However, the additional oxygen atoms in the LDPE modified bitumen or unmodified bitumen can cause a higher atomic charge due to more oxygen atoms and higher polarity. From Figure 4.11, the atomic charge is the key factor for determining the electrostatic energy and eventually improves the work of adhesion between the bitumen or LDPE modified bitumen and calcite

Compared to the unmodified bitumen-calcite interface model, LDPE modified bitumen-calcite model show a better van der Waals interaction between modified bitumen and calcite due to the introduction of five LDPE molecules using wet process. Therefore, the increased van der Waals energy leads to a smaller the distance between the modified bitumen and calcite. As a result, according to the Eq (5), the decreased distance between the bitumen and calcite increased electrostatic interaction between the LDPE modified bitumen and calcite.

As observed above, oxidative aging and LDPE have positive effects on the interfacial adhesion performance for bitumen-calcite interface models. Therefore, the work of adhesion between the bitumen and calcite can be increased after aging or adding the LDPE molecules. The adhesive energy includes van der Waals energy and coulomb electrostatic energy. The increased van der Waals energy is mainly caused by mixing 5 LDPE molecules into the virgin bitumen. However, the electrostatic energy is also increased after adding 5 LDPE molecules This is because the electrostatic energy is inversely proportional to the distance between to atoms and directly proportional to the atomic charges based on Eq (5). Therefore, the increased electrostatic energy is caused by the deceased distance between bitumen and calcite. When the LDPE modified bitumen become aged, the extra oxygen atoms results in a higher

electrostatic energy. the calcite has a relatively low wan der Waals energy with bitumen as calcite is a weak alkaline mineral. Therefore, Incorporation of LDPE molecules into bitumen seem to be less effective than oxygen atoms in bitumen in enhancing interfacial adhesion energy between the bitumen and calcite.

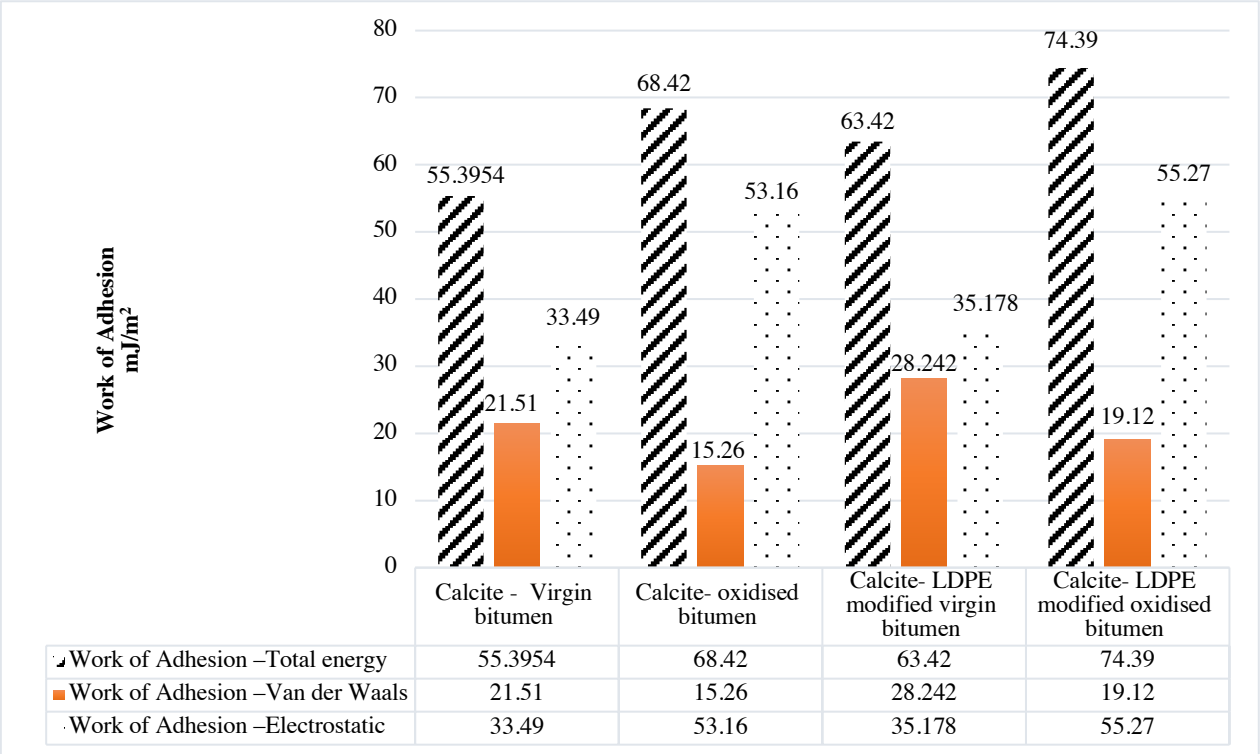
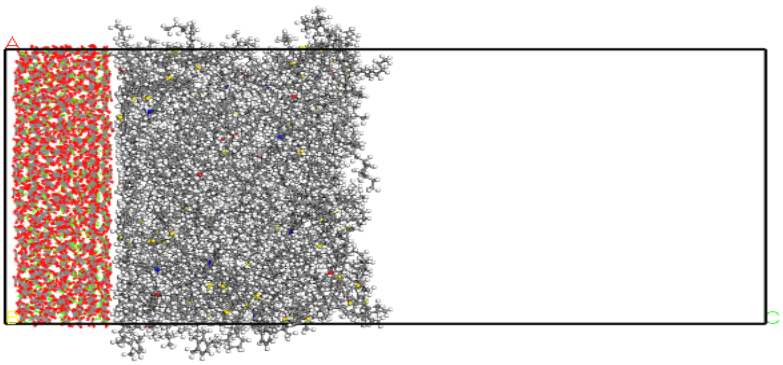
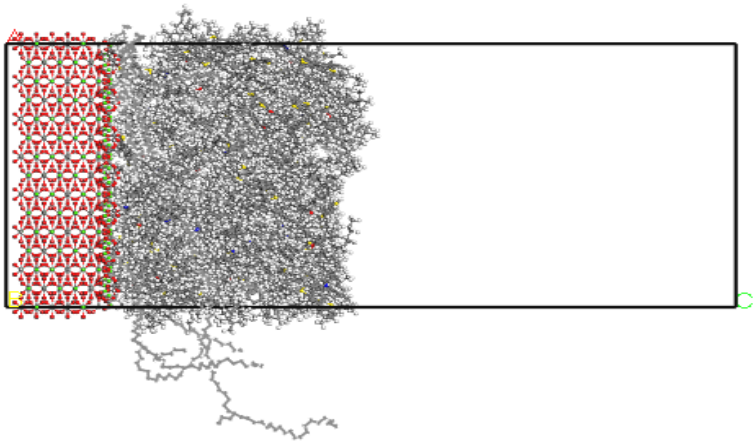
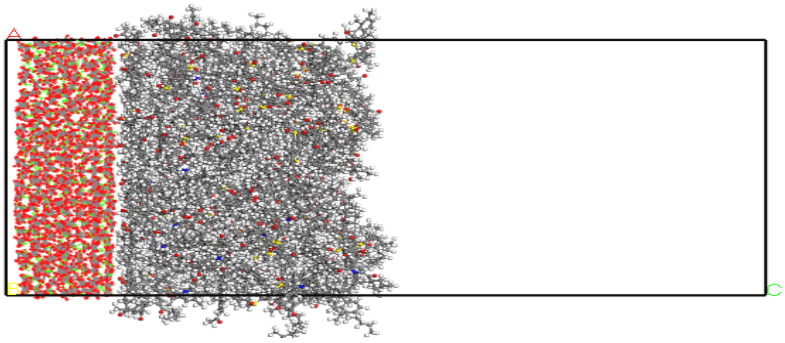
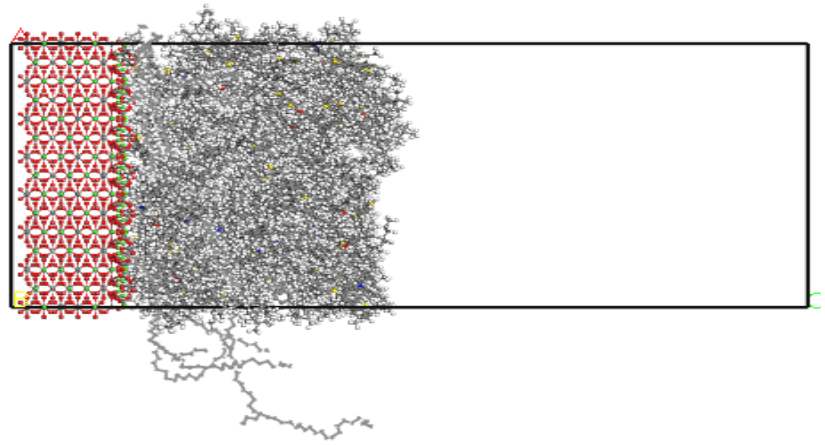


Figure 4.11 Work of adhesion of the bitumen-quartz model with or without LDPE molecules at different aging state (wet process)

Table 15. Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and Calcite matrix at different aging state (1Å= 1×10^{-10}m)- wet method.

Interface models	**Bitumen-Quartz**	**Center-to-center distance**
Virgin bitumen-Calcite		**43.03** Å
LDPE modified bitumen-Calcite		**42.09** Å
Oxidised bitumen-Calcite		**46.39** Å

LDPE modified oxidized bitumen-Calcite		**45.46** Å

(2) Combined effect of the LDPE and oxidative aging on bitumen-Calcite interface adhesion (by Dry process).

The work of adhesion for different bitumen-calcite interface models have shown in the Figure 4.12. As observed above, the interfacial adhesion performance between calcite and LDPE+Bitumen is the dominating factors that affects the interfacial adhesion performance for the Calcite-LDPE-Bitumen and main reasons dose not repeat here. Therefore, to understand interfacial adhesion performance for calcite-LDPE-oxidized bitumen, the work of adhesion between the oxidized bitumen+LDPE and calcite is analyzed. From Figure 4.12, the work of adhesion between the Calcite+LDPE and oxidized bitumen is also calculated.

As shown in the Figure 4.12, the work of adhesion between the Calcite and LDPE+ virgin bitumen is 53.77mJ/m^2 and the work of adhesion between the virgin bitumen and Calcite+LDPE is 70.71 mJ/m^2. Once the oxygen atoms are introduced into the bitumen bulk model, the work of adhesion for the Calcite + LDPE-bitumen interface model is decreased from 70.71mJ/m^2 for the virgin bitumen - Calcite+LDPE interface model to 72.71mJ/m^2 for

the oxidised bitumen - LDPE+calcite interface model. From the Figure 4.12, when the bitumen becomes aged, the greater distance between the LDPE+calcite and bitumen cause a lower electrostatic energy and higher atomic charges and eventually results in higher electrostatic energy. However, the van der Waals energy plays the main part in interfacial adhesion between the bitumen and LDPE molecules This is because, there is no interaction force between the bitumen and calcite due to the presence of 10 LDPE molecules (with thickness > 15Å). As stated above, there is no electrostatic energy between the bitumen and LDPE. Therefore, based on the Eq (4), the greater distance between the calcite+LDPE can reduce the van der Waals energy between and eventually reduce the adhesive bond energy between the bitumen and LDPE.

Whereas, the work of adhesion between calcite and LDPE+ bitumen is reduced from 53.77mJ/m^2 for calcite-LDPE+ virgin bitumen model to 50.77mJ/m^2 for calcite- LDPE+ oxidized bitumen when the additional oxygen atoms are applied into the bitumen bulk model after aging process (see Figure 4.12). As observed above, the LDPE is more likely adhere to bitumen than mineral (such as calcite). Therefore, when the bitumen becomes aged, the distance between the calcite and LDPE+bitumen is increased due to the more aggregation of bitumen molecules (higher CED value). From table 16, The distance between Calcite and LDPE + virgin bitumen model is 45.28Å and the distance between Calcite and LDPE+ oxidized bitumen is 46.28 Å. According to the Eq (4) and Eq (5), the electrostatics energy and van der are both inversely proportional to the distance between two atoms. The greater

distance leads to decrease both electrostatic energy and van der Waals energy and eventually reduce the adhesive bond energy for Calcite- LDPE + bitumen interface model after aging.

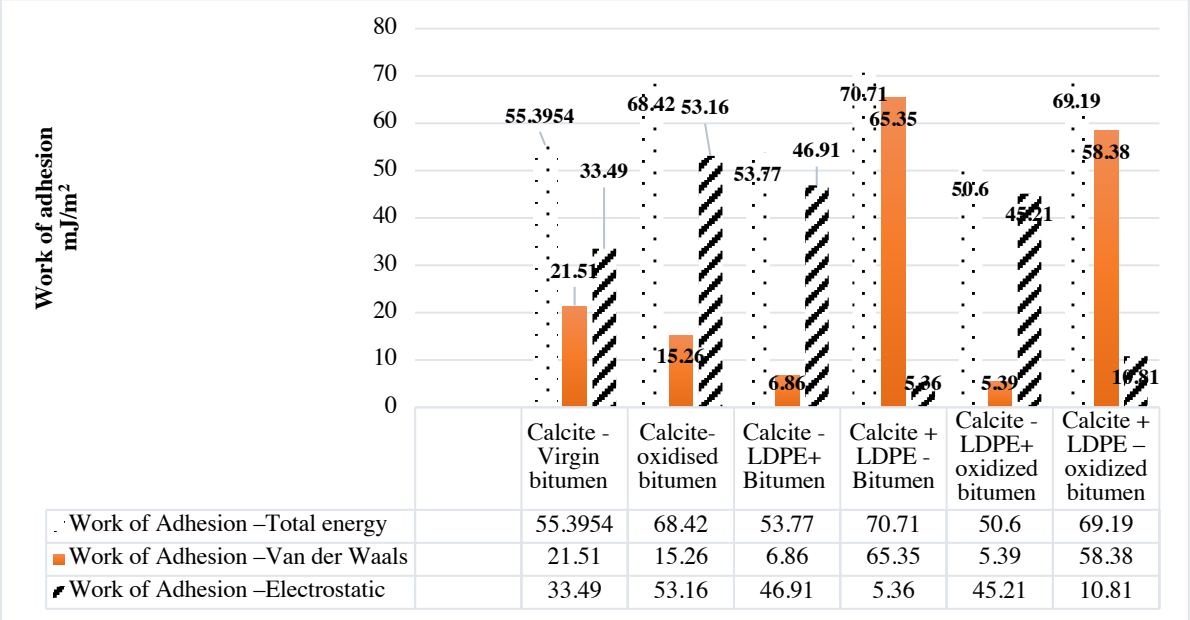
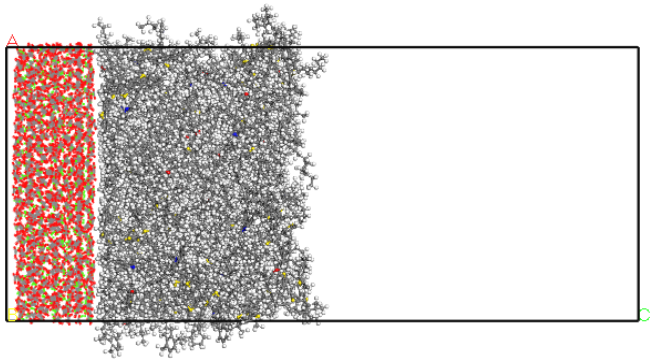
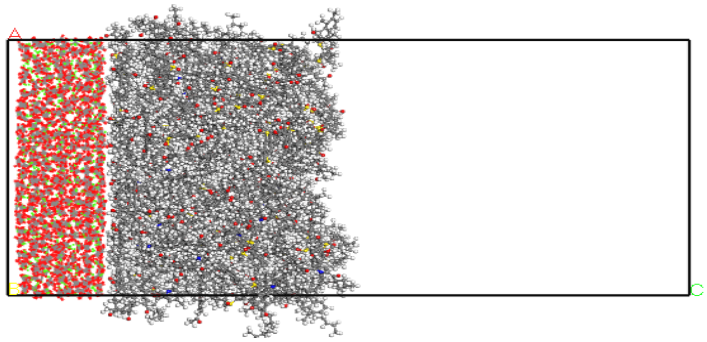
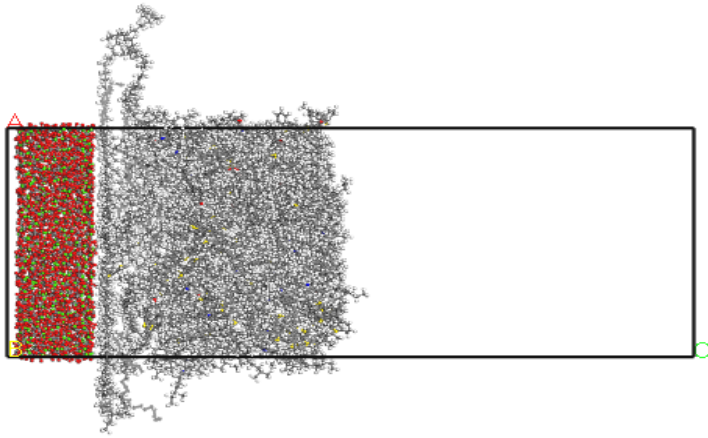
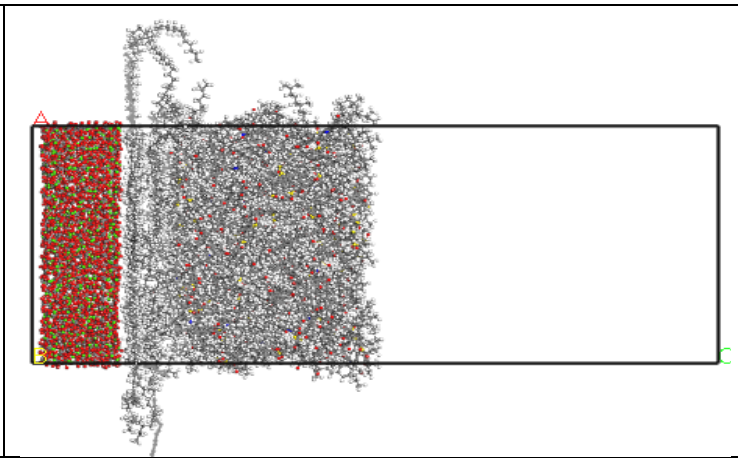


Figure 4.12 Work of adhesion of the bitumen-quartz model with or without LDPE molecules at different aging state (by Dry process)

Table 15. Center to center distance between LDPE modified bitumen mass or virgin bitumen mass and Calcite matrix at different aging state (1= 110^{-10}m)- wet method.

Interface models	Bitumen-Quartz	Center-to-center distance

Virgin bitumen-Calcite		**43.04** Å
Oxidised bitumen-Calcite		**46.39** Å
Calcite - LDPE+bitumen		**36.31** Å
Calcite+ LDPE-bitumen		**45.28** Å
Calcite - LDPE+ oxidised bitumen		**38.31** Å

Calcite+ LDPE- Oxidised bitumen		**46.28** Å

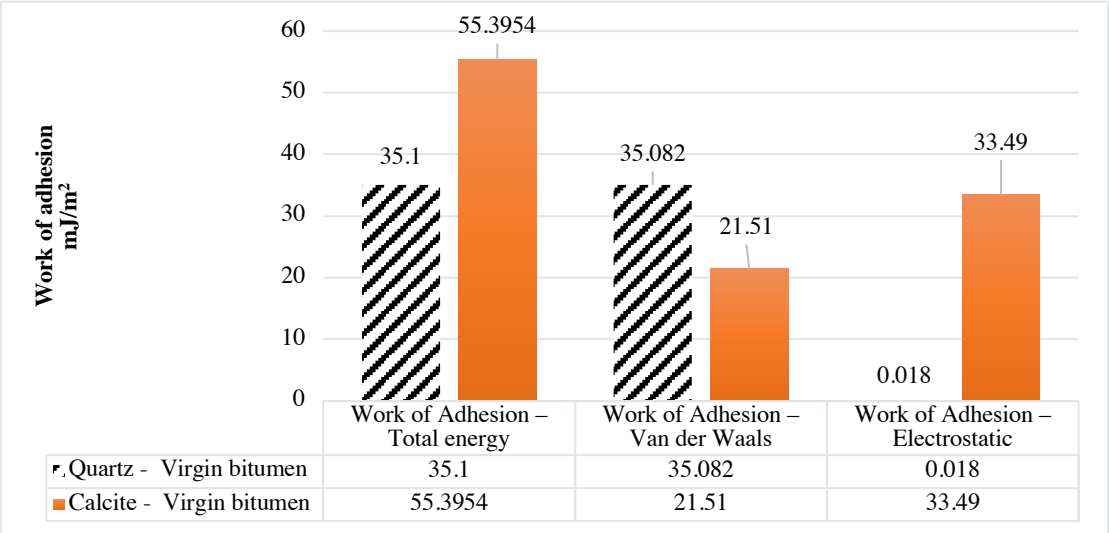
4.2.3 The Effect of different mineral types on work of adhesion

In this study, the effect of different minerals on interface adhesion performance in pavement is investigated using the MD simulations. According to the Eq (3), the non-bond energy includes van der Waals energy and electrostatic energy, the energy components which attribute to the work of adhesion between mineral and bitumen is shown in the Figure 4.13.

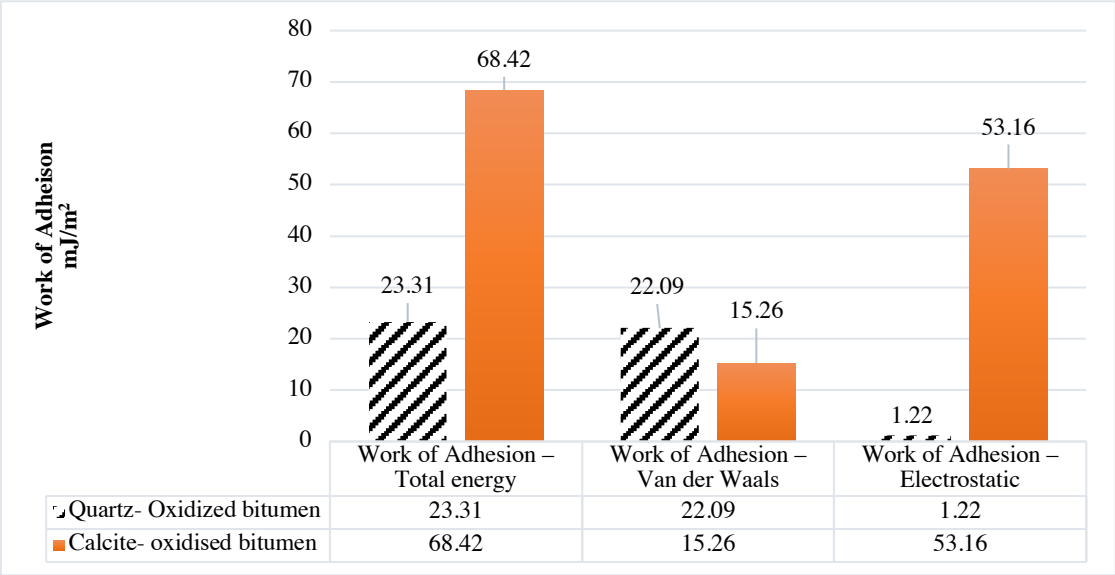
The Figure 4.13(a) shows the bitumen and quartz interact with each other mainly by van der Waals energy. However, compared to the virgin bitumen-quartz interface models, the electrostatic energy is a major part for interfacial adhesion energy between the virgin bitumen and calcite. As shown from the Figure 4.13 (b) to Figure 4.13 (c), the van der Waal energy is still a primary contributor to the total energy for quartz-bitumen interface models and the electrostatic energy is still takes up a major part in calcite-bitumen interface models regardless of whether the bitumen is affected by the LDPE and oxidative aging or not. These results are consistent with the simulation results (Gao et al ,2018, Xie et al ,2019). As stated above, the quartz is an electronically natural mineral, having a very weak electrostatic interaction with bitumen so that the van der Waals becomes the major part for the adhesion

between the quartz and acidic bitumen. Unlike the bitumen-quartz interface model, the electrostatic energy is the primary contributor for the adhesion between the calcite and bitumen. This is because the calcite is a weak alkali mineral. This finding also reported by Mirzababaer (2011) that aggregate have a large amount of calcite mineral shows a strong electrostatic adhesion between the bitumen and calcite.

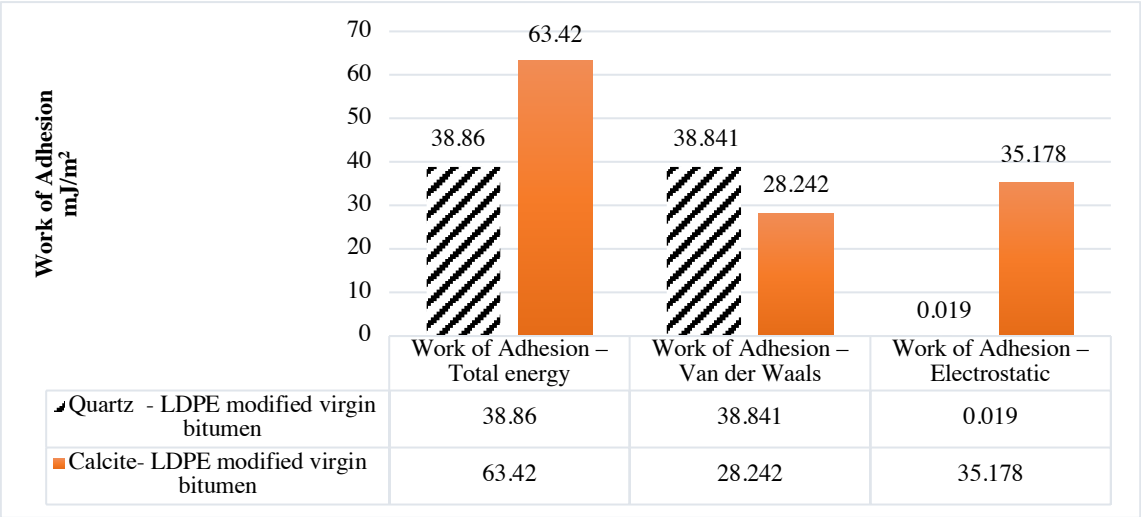
Compared to the bitumen-quartz interface models, the interfacial adhesion energy between the bitumen and calcite is much greater (see Figure 4.12). For example, the work of adhesion for the virgin bitumen-quartz is 35.1mJ/m^2 and the work of adhesion for virgin bitumen-calcite is 55.40mJ/m^2. Moreover, the work of adhesion for quartz-LDPE modified bitumen model (74.39mJ/m^2) is much higher than the work of adhesion for calcite-LDPE modified bitumen model (33.97 mJ/m^2). Therefore, the ranking for the adhesion energy between acidic bitumen and two minerals is as follow: calcite>quartz. These results can be explained by the acid-base theory. This is because, considering the content of heteroatoms such as Sulphur, oxygen in bitumen is very small, the bitumen is always acid material. Therefore, acid material easily adheres to alkaline material such as calcite mineral with strong strength, while the quartz is acid mineral so there is a relatively weak adhesive bond energy between the acid bitumen and acid quartz. This conclusion is in agreement with the previous study from Cuclan (2019). Therefore, in other words, the electrostatic energy is more helpful than van der Waals energy to improve the adhesive energy and the interaction between bitumen and minerals



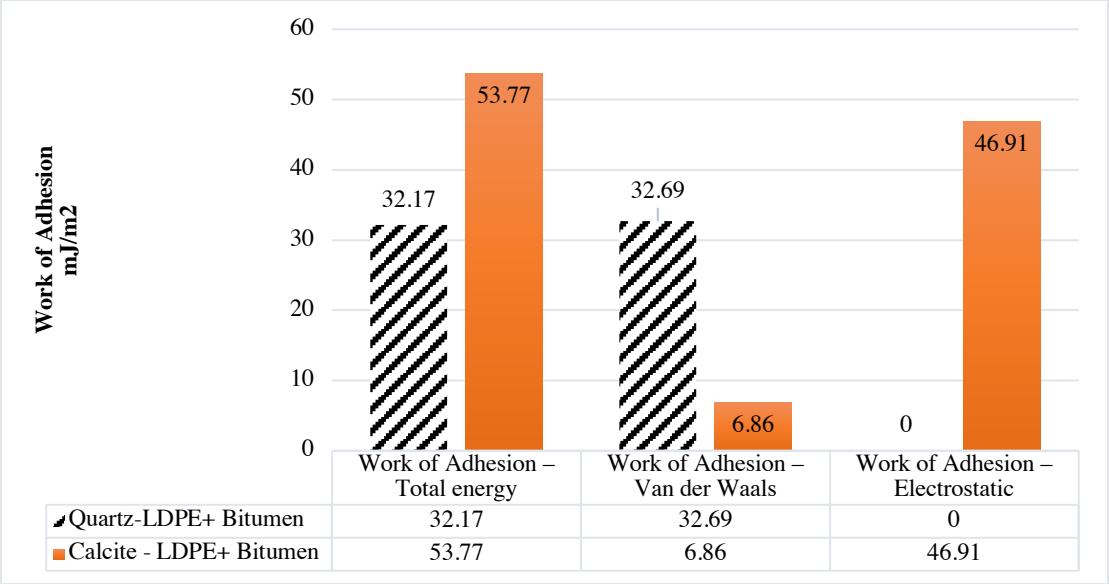
(a) Quartz-virgin bitumen model and Calcite-virgin bitumen model



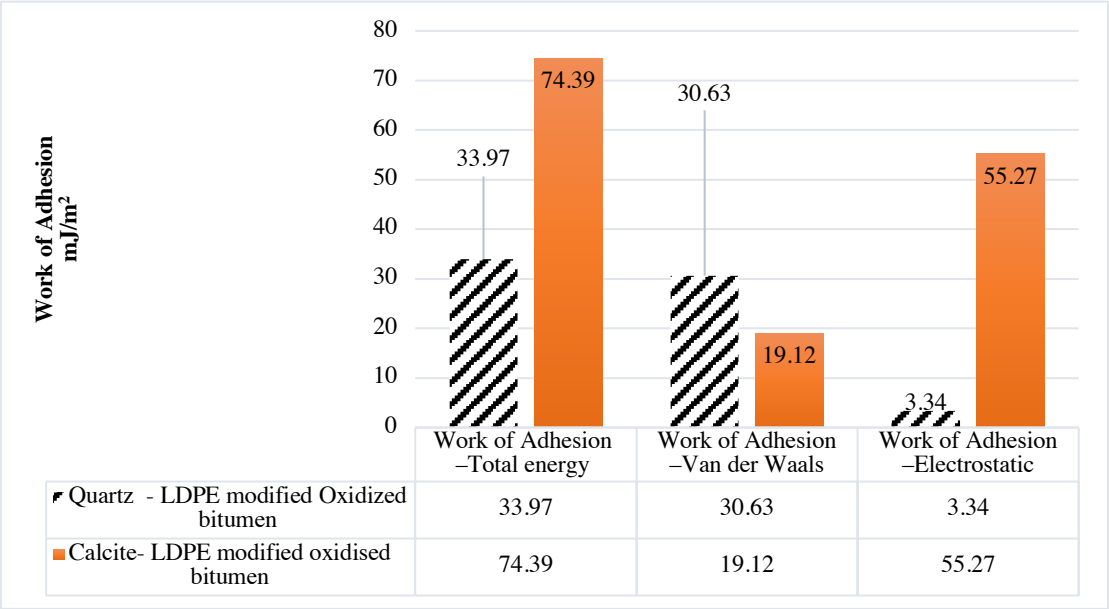
(b) Quartz-oxidized bitumen model and Calcite-oxidized Bitumen model



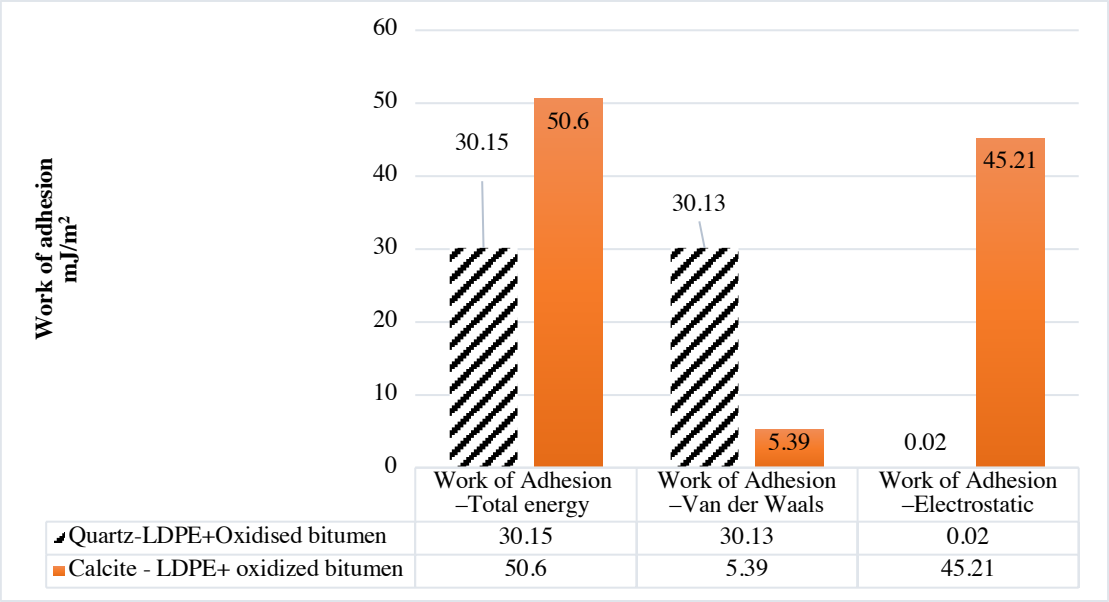
(c) Quartz- LDPE modified bitumen model and Calcite-Bitumen model (wet method).



(d) Quartz-LDPE+ bitumen model and Calcite-LDPE+ bitumen model (dry method).



(e) Quartz- LDPE modified oxidized bitumen model and Calcite-Bitumen oxidized model (wet method).



(f) Quartz-LDPE+ oxidized bitumen model and Calcite-LDPE+ oxidized bitumen model (dry method).

Figure 4.13, Contribution of non-bond components including van der Waals and electrostatic energy to the work of adhesion for two different mineral-bitumen systems.

4.3 Data Analysis and Discussion Summary

The adhesion work for calcite- bitumen interface models and quartz-bitumen interface models are calculated in different conditions. The main conclusion can be drawn as follows:

1) The interfacial adhesion energy is composed of non-bond energy. Van der Waals force is the main contribution for adhesion performance between bitumen and quartz. For calcite, electrostatic force is dominant in the interface adhesion.
2) The oxidative aging has a negative effect on the quartz-bitumen interfacial adhesion performance. However, the oxidative aging has a positive effect on the calcite-bitumen interfacial adhesion performance.
3) The incorporation of LDPE into the bitumen using wet process can increase the van der Waals bond energy between mineral and bitumen, which can further increase the adhesive bond energy between mineral and bitumen eventually.
4) The interfacial adhesion performance for mineral-LDPE-Bitumen models are determined by the adhesive performance between the mineral and LDPE+bitumen instead of by the adhesive performance between the Mineral + LDPE and bitumen.
5) Calcite-bitumen interface models has a better adhesion performance than quartz-bitumen combination regardless the effects of oxidative aging and LDPE.

Chapter 5 Conclusion and Recommendation

5.1 Summary and Conclusions

In this thesis, the effects of mineral types, oxidative levels and LDPE processing method (dry and wet process) on the interface adhesion performance in asphalt materials were studied using molecular dynamics (MD) simulations.

The bitumen at different oxidation levels were used for modelling the interface with quartz and calcite to investigate the effects of the oxidative levels on the interfacial adhesion performance between bitumen and minerals. In addition, LDPE molecules are introduced into the model by using two different methods (dry method& wet method) to investigate the effects of LDPE on the interfacial adhesion performance between bitumen and mineral surfaces. Finally, the LDPE molecules were introduced into the model after aging to understand the combined effects of LDPE and oxidative aging on the interfacial adhesion between mineral and bitumen.

The following conclusions are drawn from the results of this study.

1. Cohesive energy density (CED) can be used to analysis the intermolecular bonding strength of bitumen. The cohesive energy density includes van der Waals energy and electrostatic energy. When the bitumen becomes aged, the cohesive energy of bitumen is increased, which results in the aggregation of bitumen molecules. The increased CED value is fundamentally caused by the increased van der Waals energy and electrostatic energy. This is because, the additional oxygen atoms cause higher molecular weight and

higher polarity than that of virgin bitumen. Moreover, the bitumen is mainly composed of hydrocarbon molecules which are mainly non-polar. Therefore, the cohesive energy of bitumen is dominated by van der Waals interaction. Finally, the presence of 5 LDPE molecules (9%wt) in bitumen can help to enhance the intermolecular bond strength of bitumen regardless of whether the bitumen is oxidized or not.

2. The interfacial adhesive energy between mineral and bitumen is composed of non-bond energy including van der Waals interactions and electrostatic force. Van der Waals interaction plays the primary contribution for the adhesion between the bitumen with acidic mineral such as quartz. Whereas, for bitumen-alkaline mineral, the electrostatic force dominates the interface adhesion,
3. For bitumen-quartz interfaces, the interfacial adhesive energy is decreased when the bitumen becomes aged. This is due to the increased distance between the bitumen and quartz caused by the aggregated bitumen during the ageing process. However, for bitumen-calcite combination, the adhesive bond energy between the bitumen and calcite is increased when the bitumen become aged. This is because the higher oxidation level results in higher atomic chargers in the bitumen and therefore higher electrostatic energy between the calcite and bitumen. As a result, the higher oxidation level in the bitumen can decrease the interfacial adhesion between the bitumen and acid mineral like quartz, while the interfacial adhesion between the bitumen and alkali mineral such as calcite can be enhanced when the bitumen becomes aged. In conclusion, the oxidative aging is beneficial to enhance the interfacial adhesion between the bitumen and alkaline mineral. Limitations of this conclusion come from that when the ageing becomes further severe

the interfacial adhesion between the bitumen and the alkaline minerals can be reduced due to the bitumen's aggregation. In addition, the moisture is not considered in the modelling.

4. When the LDPE are introduced into the bitumen by wet process, the work of adhesion is increased for both the bitumen-quartz model and the bitumen-calcite model. However, this enhancement of the adhesion due to the addition of the LDPE molecules in the heavily oxidized bitumen is not as remarkable as that for the unaged bitumen, which may be related to the low content of LDPE are introduced into the asphalt binder and the oxidation has dominated the adhesion between the bitumen and the mineral surfaces. In sum, the incorporation of LDPE into the asphalt binder by wet process is beneficial to improve the interface adhesion performance of asphalt pavement.
5. When the LDPE molecules is introduced bitumen by dry method, the work of adhesion for bitumen-LDPE-mineral system is dominated by the interfacial adhesion performance between the LDPE and bitumen no matter if the bitumen is oxidized or not. This is because the adhesion of the LDPE-mineral interface is stronger than that of the bitumen-LDPE interface. Therefore, the incorporation of LDPE into the bitumen by a dry method has a negative effect on the interface adhesion performance between the mineral and bitumen. This is because, the adhesive bond energy between the mineral and LDPE is much smaller than the adhesive bond energy bitumen and mineral.
6. The adhesion energy between calcite and bitumen is much higher than that of quartz regardless of the effect of LDPE and oxidative aging. This is because, the calcite is more likely to adhere to bitumen than quartz due to its higher polarity. Additionally, the van

der Waals energy constitutes in a major part in quartz-bitumen interface adhesion bitumen, while the electrostatic energy is the key factor determining the adhesion energy between the calcite and bitumen. Furthermore, compared to the effect of LDPE on adhesion, the effect of oxidative aging on adhesion is the dominating factor in determining the adhesion performance in the system. LDPE can only improve the van der Waals interaction for mineral-bitumen model.

5.2 Recommendation for further study

- The validation of the simulation results is limited to using the results and findings from the existing studies in the literature. Laboratory tests for validating the conclusions from the molecular dynamic simulations need to be included in the future study when the Covid-19 disappears. This can help to improve the reliability of the results and increase the validity of data.
- More MD modelling could be included by introducing the moisture and higher ageing severity to evaluate how the adhesion is changed due to the ageing and the addition of the LDPE using dry and wet methods.
- The computational power is limited so the duration of simulation is limited up to 200ps. However, the longer duration of simulation can make the results for work of adhesion better representing the real material behavior.
- There are few or no previous studies on LDPE modified asphalt by MD simulations. Specifically, the LDPE molecules used in this study still need to be improved to obtain a more realistic representation of the LDPE.

- Another recommendation is to increase the proportion of LDPE. In this study, the incorporation the LDPE into the bitumen seems to be less effective than the oxidative aging in influencing interfacial adhesion energy, which may be related to the low percentage of LDPE (max 18%) used in the study.
- The last recommendation is to study the interfacial adhesion performance between acidic bitumen and strong alkaline mineral (such as albite). It can help to understand if the additives such as LDPE can mitigate the effect of oxidation within the bitumen on the work of adhesion between the bitumen and strong alkaline.

References

Adhesive.org 2010, Adhesion and cohesion, The Adhesive and Sealant Council Inc.: Maryland, retrieved November 17, 2010, from http://www.adhesives.org/training education/student resources/adhesionandcohesion.aspx

Aguiar-Moya, J. P., Salazar-Delgado, J., Baldi-Sevilla, A., Leiva-Villacorta, F., & Loria-Salazar, L. (2015). Effect of aging on adhesion properties of asphalt mixtures with the use of bitumen bond strength and surface energy measurement tests. Transportation Research Record: Journal of the Transportation Research Board, 2505(1), 57–65. https://doi.org/10.3141/2505-08

Allen, Mike P., and Dominic J. Tildesley. Computer simulation of liquids. Oxford university press, 1989.

Artok, Levent, Yan Su, Yoshihisa Hirose, Masahiro Hosokawa, Satoru Murata, and Masakatsu Nomura. "Structure and reactivity of petroleum-derived asphaltene." Energy & Fuels 13, no. 2 (1999): 287-296.

Anderson, DA, Christensen, DW, Bahia, HU, Dongre, R, Sharma, MG, Antle, CE & Button, J 1994, Binder characterisation and evaluation. Volume 3: Physical characterisation: Strategic Highway Research Program Report A-369, National Research Council: Washington DC.

Andersen, H. (1980). Molecular dynamics simulations at constant pressure and/or temperature. The Journal of Chemical Physics, 72(4), 2384-2393.

Asphalt Institute 2007, Minimizing moisture sensitivity, Asphalt Institute: Lexington, retrieved February 28, 2008, from http://www.asphaltmagazine.com/singlenews .asp?item_ID=1348&comm=0&list_code_int=MAG01-INT

AZO Materias, 2012. Polystyrene (PS)(C_8H_8) Plastic Recycling.

Babalghaith, A., Koting, S., Ramli Sulong, N., & Karim, M. (2019). Optimization of mixing time for polymer modified asphalt. IOP Conference Series: Materials Science And Engineering, 512, 012030.

Bhasin, Amit, Rammohan Bommavaram, Michael L. Greenfield, and Dallas N. Little. "Use of molecular dynamics to investigate self-healing mechanisms in asphalt binders." Journal of Materials in Civil Engineering 23, no. 4 (2010): 485-492.

B. Singh, Lokesh Kumar, M. Gupta, G. S. Chauhan, Polymer-Modified Bitumen of Recycled LDPE and Malleated Bitumen. APPL. POLYM. SCI.2013, 67-78.

Boysen, R. and J. Schabron, Laboratory and Field Asphalt Binder Aging: Chemical Changes and Influence on Asphalt Binder Embrittlement. Federal Highway Administration, Report No. FHWA-HRT-11-045, McLean, VA, 2015.

Bhasin,A, Masad,E little,D,Lytton,R 2006, 'Limits on adhesive bond energy for improved resistance of hot mix asphalt to moisture-damage', paper presented to the Transportation Research Board 85th Annual Meeting, Washington DC, January 22-26, 2006.

Blackman,BRK,Kinloch,AJ,Taylor,AC&Wang,Y 2000, 'The impact wedge-peel performance of structural adhesive', Journal of Materials Science, vol. 35, pp. 1867-1884.

British Standard Institution 1999, Products and systems for the protection and repair of concrete structures-Test Methods-Measurement of bond strength by pull-off, BS EN 1542:1999, British Standards Institution: London.

British Standard Institution 2001, Determination of the mode I adhesive fracture energy GIC of structure adhesives using the double cantilever beam (DBC) and tapered double cantilever beam (TDCB) specimens, BS 7991:2001, British Standards Institution: London.

British Standard Institution 2003, Paints and varnishes-Pull-off test for adhesion, BS EN ISO 4624:2003 BS 3900-E10:2003, British Standards Institution: London.

Brasileiro, Luzana & Moreno-Navarro, Fernando & Tauste, Raúl & Matos, Jose & Gámez, Ma. (2019). Reclaimed Polymers as Asphalt Binder Modifiers for More Sustainable Roads: A Review. Sustainability. 11. 646. 10.3390/su11030646.

Brûlé, B. (1996). Polymer-Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles. Transportation Research Record: Journal of The Transportation Research Board, 1535(1), 48-53. doi: 10.1177/0361198196153500107

Chang, WV 1994, Application of acoustic emission to study the cohesive and adhesive strength of asphalt: Strategic Highway Research Program Report A-682, National Research Council: Washington DC.

Cheng, D, Little,DN,Lytton,RL&Holste,JC 2002, 'Use of surface free energy of asphalt-aggregate system to predict moisture-damage potential' Journal of the Association of Asphalt Paving Technologists, vol. 71, pp. 59-88.

Cimatti, B., Campana, G., & Carluccio, L. (2017). Eco Design and Sustainable Manufacturing in Fashion: A Case Study in the Luxury Personal Accessories Industry. *Procedia Manufacturing*, *8*, 393-400.

Corbett, L. W. (2002). Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution- adsorption chromatography, and densimetric characterization. Analytical Chemistry, 41(4), 576–579. https://doi.org/ 10.1021/ac60273a004

Copeland, AR 2007, 'Influence of moisture on bond strength of asphalt-aggregate systems', PHD thesis, Vanderbilt University,Nashville,Retrieved August 2, 2008.

Cordon, WA 1979, Properties, Evaluation and Control of Engineering Materials, McGraw-Hill: New York.

Claudy, P., Letoffe, J. M., King, G. N., and Plancke, J. P. (1992). "Characterization of Asphalts Cements by Thermomicroscopy and Differential Scanning Calorimetry: Correlation to Classic Physical Properties." Fuel Science and Technology International, Taylor & Francis, 10(4-6), 735–765.

Corbett, Luke W. "Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography, and densimetric characterization." Analytical Chemistry 41, no. 4 (1969): 576-579.

Colin Hindle, Edinburgh Napier University. 'Polypropylene.' British Plastics Federation. 2019.

Cui, J., Wang, R., Sinclair, A., & Spelt, J. (2003). A calibrated finite element model of adhesive peeling. International Journal of Adhesion And Adhesives, 23(3), 199-206. doi: 10.1016/s0143-7496(03)00012-5

Cui, S, Backman, BRK, Kinloch, AJ & Taylor,AC 2010, ' Fracture tests of asphalt joints', slide presented to the 3rd Engineering and Physical Sciences Research Council (EPSRC) Meeting, Nottingham, February 11, 2010.

Curtis, C. W., Ensley, K., & Epps, J. (1993). Fundamental properties of asphalt-aggregate interactions including adhesion and absorption (No. SHRP-A-341). National Research Council.

Daly, William H., Ioan I. Negulescu, and Ionela Glover. "A comparative analysis of modified binders: original asphalts and materials extracted from existing pavements." Federal Highway Administration Report No. FHWA/LA 10 (2010): 462

Deng, Y. J., Dixon, J. B., Dixon, J. B., & Schulze, D. G. (2002). Soil organic matter and organic-mineral interactions. Soil Mineralogy with Environmental Applications, 69–107. https://doi.org/10.2136/sssabookser7.c3

Denning, J., & Carswell, J. (1981). Improvements in rolled asphalt surfacings by the addition of organic polymers. Crowthorne, Berkshire: Transport and Road Research Laboratory.

Department for Transport 2009, Transport statistics Great Britain 2009 35th edition, TSO Publications: London.

DFD Instruments n.d., ASTM D4541 and ISO 4624 Adhesion testing standards used together with PAT testers from DFD® Instruments, DFD Instruments: Surrey, United Kingdom, retrieved January 9, 2008, from http://www.dfdinstruments.co.uk/topics/Study5-ASTM-D4541.htm.

Dong, M. S., Gao, Y. M., Li, L. L., Wang, L. N., & Sun, Z. B. (2016). Viscoelastic micromechanical model for dynamic modulus prediction of asphalt concrete with interface effects. Journal of Central South University, 23(4), 926–933. https://doi.org/10.1007/s11771-016-3140-y

Ding, Yongjie, Boming Tang, Yuzhen Zhang, Jianming Wei, and Xuejuan Cao. "Molecular Dynamics Simulation to Investigate the Influence of SBS on Molecular Agglomeration Behavior of Asphalt." Journal of Materials in Civil Engineering 27, no. 8 (2013): C4014004.

Ding, Yongjie, Baoshan Huang, Xiang Shu, Yuzhen Zhang, and Mark E. Woods. "Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders." Fuel 174 (2016): 267-273.

Fallah, F., Khabaz, F., Kim, Y. R., Kommidi, S. R., & Haghshenas, H. F. (2019). Molecular dynamics modeling and simulation of bituminous binder chemical aging due to variation of oxidation level and saturate-aromatic-resin-asphaltene fraction.Fuel, 237, 71–80. https://doi.org/10.1016/j.fuel.2018.09.110

Fromm,HJ 1974, ' The mechanisms of asphalt stripping from aggregates surfaces' Journal of the Association of Asphalt Paving Technologists, vol. 43, pp. 191-223.

Gao, Y., Zhang, Y., Gu, F., Xu, T., & Wang, H. (2018). Impact of minerals and water on bitumen-mineral adhesion and debonding behaviors using molecular dynamics simulations. Construction and Building Materials, 171, 214–222. https://doi.org/10.1016/j.conbuildmat.2018.03.136

Ghuzlan, K., Al-Khateeb, G., & Damrah, A. (2013). Using oil shale ash waste as a modifier for asphalt binders. Journal of Material Cycles And Waste Management, 15(4), 522-529.

Gong, M., Zhu, H., Pauli, T., Yang, J., Wei, J., & Yao, Z. (2017). Evaluation of bio-binder modified asphalt's adhesion behavior using sessile drop device and atomic force microscopy. Construction and Building Materials, 145, 42–51. https://doi.org/10.1016/j.conbuildmat.2017.03.114

Grenfell, J., Ahmad, N., Liu, Y., Apeagyei, A., Large, D., & Airey, G. (2014). Assessing asphalt mixture moisture susceptibility through intrinsic adhesion, bitumen stripping and mechanical damage. Road Materials and Pavement Design, 15(1), 131–152. https://doi.org/10.1080/14680629.2013.863162

Greenfield, Michael L. "Molecular modelling and simulation of asphaltenes and bituminous materials." International Journal of Pavement Engineering 12, no. 4 (2011): 325-341.

Groenzin, Henning, and Oliver C. Mullins. "Molecular size and structure of asphaltenes from various sources." Energy & Fuels 14, no. 3 (2000): 677-684.

Hansen, Jesper Schmidt, Claire A. Lemarchand, Erik Nielsen, Jeppe C. Dyre, and Thomas Schrøder. "Four-component united-atom model of bitumen." The Journal of chemical physics 138, no. 9 (2013): 094508.

Hadavinia, H., Kawashita, L., Kinloch, A., Moore, D., & Williams, J. (2006). A numerical analysis of the elastic-plastic peel test. *Engineering Fracture Mechanics*, *73*(16), 2324-2335.

Harrison, N., & Harrison, W. (1972). The Stresses in an Adhesive Layer. *The Journal Of Adhesion*, *3*(3), 195-212. doi: 10.1080/00218467208072193

Harvey, J., & Cebon, D. (2005). Fracture Tests on Bitumen Films. Journal of Materials in Civil Engineering, 17(1), 99-106. doi: 10.1061/(asce)0899-1561(2005)17:1(99)

Harvey, JAF,2000, 'Bitumen films in tension', PHD Thesis, University of Cambridge, Cambridge,England.

Heavens, O. (1950). Some factors influencing the adhesion of films produced by vacuum evaporation. Journal De Physique Et Le Radium, 11(7), 355-360.

Hicks, RG 1991, Moisture damage in asphalt concrete: NCHRP Synthesis of Highway Practice Vol. 175, Transportation Research, Transportation Research Board and National Research Council: Washington DC.

Holownia, B. (1972). Effect of Poisson's ratio on bonded rubber blocks. Journal of Strain Analysis, 7(3), 236-242. doi: 10.1243/03093247v073236

Hoover, W. (1985). Canonical dynamics: Equilibrium phase-space distributions. Physical Review A, 31(3), 1695-1697. doi: 10.1103/physreva.31.1695

Huang, SC, Branthaver, JF & Robertson, RE 2000, 'Effects of Aggregate on asphalt-aggregate interaction', in 8th Annual Symposium of the International Centre for Aggregate Research (ICAR), Denver, Colorado, April 12-14, 2000, International Center for Aggregates Research, University of Texas: Texas, pp. 1-20.

Huang, SC, Turner, TF, Pauli, AT, Miknis, FP, Branthaver, JF & Robertson, RE 2005, 'Evaluation of different techniques for adhesive properties of asphalt-filler systems at interfacial region', in Damico (ed.), Adhesives, Adhesion Science and Testing: ASTM Special Technical Publication No. 1463, Washington DC,October 4, 2004, American Society for Testing and Materials: Philadelphia, pp. 114-128.

Huang,X 2005, 'Analytical techniques for characterising asphalt-aggregate mixture system', Slide presented to the 13th Conference of Pavement Engineering, Chuang Hua University, Taiwan, October 2005.

Huang, YS 2004, Pavement analysis and design, 2nd edn, Pearson/Prentice Hall: New Jersey

Hughes, CS & Maupin, GW, Jr. 1989, 'Factors that influence moisture damage in asphaltic pavements,' In HG Schreuders & CR Marek (eds), Implication of Aggregates in the Design, Construction and Performance of Flexible Pavements: ASTM Special Technical Publication No. 1016, New Orleans, Louisiana, December 3, 1986, American Society for Testing and Materials: Philadelphia, pp. 96-102.

Infoplease 2008, United Kingdom: History, geography, government and culture, Pearson Education: Boston, retrieved February 25, 2008, from http://www.info please.com/ipa/A0108078.html

IKA Bitumen. (2019). Retrieved 24 October 2020, from https://www.ikaprocess.com/en/Industry/Bitumen-cip-5.html

Johnson, DR & Freeman, RB 2002, Rehabilitation techniques for stripped asphalt pavements: FHWA/MT-002-003/8123, Western Transportation Institute: Bozeman, Montana.

Johnston, C. T., & Tombacz, E. (2002). Surface chemistry of soil minerals. In S. Dixon (Ed.), Soil mineralogy with environmental applications (pp. 37–68). Soil Science Society of America, Inc.

Kandhal, P1994, "Field and laboratory investigation of stripping in asphalt pavements: State of the art report, Journal of the Transportation Research Board, vol. 1454, pp. 36-47.

Kandhal, PS & Rickards, IJ 2001, Premature failure of asphalt overlays from stripping: Case Histories: NCAT Report 01-01, National Center for Asphalt Technology (NCAT): Auburn University, Auburn.

Kanitpong,K & Bahia, HU 2003, 'Role of adhesion and thin film tackiness of asphalt Binders in moisture damage of HMA', Journal of the Association of Asphalt Paving Technologists, vol. 72, pp. 611-642.

Kanitpong,K & Bahia, HU 2003, 'Sensitivity of moisture damage of HMA asphalt binder cohesion and adhesion properties', in 17th ASCE Engineering Mechanics Conference, University of Delaware, Newark, June 13-16, 2004, University of Delaware: Newark DE, pp. 1-13.

Kanitpong,K & Bahia, HU 2003, 'Relating adhesion and cohesion of asphalts to the effect of moisture on laboratory performance of asphalt mixtures', Journal of the Transportation Research Board, vol. 1901, pp. 33-43.

Kendall, K 1971, 'The adhesion and surface energy of elastic solids', Journal of Physics D: Applied Physics, vol. 4, no. 8, pp. 1186-1195.

Kennedy, TW, Roberts, FL & Kang, WL 1982, 'Evaluation of moisture susceptibility of asphalt mixtures using the Texas Freeze- Thaw Pedestal test', Journal of the Association of Asphalt Paving Technologists, vol. 51, pp. 327-341.

Kiggundu, BM & Roberts, FL 1988, Stripping in HMA mixture: State-of-the-art and critical review of test methods: NCAT Report 88-2, National Center for Asphalt Technology (NCAT): Auburn University, Auburn.

Kim, S & Coree, BJ 2005, Evaluation of Hot Mix Asphalt moisture sensitivity using the Nottingham Asphalt Test equipment: IHRB Project TR-483, Centre for Transportation Research and Education: Iowa State University, Iowa.

Kinloch, AJ 1982, 'Review the science of adhesion: Part 2 Mechanics and mechanisms of failure', Journal of Materials Science, vol. 17, pp. 617-651.

Kinloch, AJ 1987, Adhesion and adhesives science and technology, Chapman and Hall: London and New York.

Kinloch, AJ 1997, 'Adhesives in engineering,' Proceedings of the I MECH E Part G Journal of Aerospace Engineering, vol. 211, pp. 307-335.

Khabaz, Fardin, and Rajesh Khare. "Glass transition and molecular mobility in styrene– butadiene rubber modified asphalt." The Journal of Physical Chemistry B 119, no. 44 (2015): 14261-14269.

Kriz, Pavel, Jiri Stastna, and Ludo Zanzotto. "Glass transition and phase stability in asphalt binders." Road Materials and Pavement Design 9, no. sup1 (2008): 37-65.

Labib, ME 1992, 'Asphalt-aggregate interactions and mechanisms for water stripping', American Chemical Society Division of Fuel Chemistry vol. 37, no. 3, pp. 1472-1481.

Lemarchand, Claire A., Thomas B. Schrøder, Jeppe C. Dyre, and Jesper S. Hansen. "Cooee bitumen: Chemical aging." The Journal of chemical physics 139, no. 12 (2013): 124506.

Lesueur, Didier. "The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification." Advances in colloid and interface science 145, no. 1 (2009): 42-82.

Liebman, S. A. and Levy, E. J., "Pyrolysis and GC in Polymer Analysis~'MARCNL DEKKER,/NC., 156 (1985).

López, A., de Marco, I., Caballero, B., Adrados, A., & Laresgoiti, M. (2011). Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. *Waste Management*, *31*(8), 1852-1858.

Li, Derek D., and Michael L. Greenfield. "Chemical compositions of improved model asphalt systems for molecular simulations." Fuel 115 (2014): 347-356.

Li, R., Du, H., Fan, Z., & Pei, J. (2016). Molecular dynamics simulation to investigate the interaction of asphaltene and oxide in aggregate. Advances in Materials Science and Engineering, 2016. https://doi.org/10.1155/2016/3817123

Li, D. D., & Greenfield, M. L. (2014). Chemical compositions of improved model asphalt systems for molecular simulations. Fuel, 115(1), 347–356. https://doi.org/10.1016/j.fuel.2013.07.012

Lu, Y., & Wang, L. (2017). Atomistic modelling of moisture sensitivity: A damage mechanisms study of asphalt concrete interfaces. Road Materials and Pavement Design, 18(sup3), 200–214. https://doi.org/10.1080/14680629.2017.1329875

Lu, Y., & Wang, L. (2011). Nano-mechanics modelling of deformation and failure behaviours at asphalt–aggregate interfaces. International Journal of Pavement Engineering, 12(4), 311-323. doi: 10.1080/10298436.2011.575136

Lytton, RL, Masad, EA, Zollinger, C, Bulut, R & Little, D 2005, Measurements of surface energy and its relationship to moisture damage: FHWA/TX-05/0-4524-2, Texas Transportation Institute: College Station, Texas.
Mack, C 1957, 'Physical properties of asphalt in thin films,' Industrial Engineering Chemistry, vol. 49, p. 422.

María A. Vargas, Miguel A. Vargas, Antonio Sánchez-Sólis, Octavio Manero, Asphalt/polyethylene blends: Rheological properties, microstructure and viscosity modeling, Construction and Building Materials, Volume 45, 2013, Pages 243-250, ISSN 0950-0618.

Martín-Martínez, F. J., Fini, E. H., & Buehler, M. J. (2015). Molecular asphaltene models based on Clar sextet theory. RSC Advances, 5(1), 753–759. https://doi.org/10.1039/C4RA05694A

Marcilla, A., Beltrán, M., & Navarro, R. (2009). Evolution of products during the degradation of polyethylene in a batch reactor. Journal of Analytical And Applied Pyrolysis, 86(1), 14-21.

Majidzadeh, K & Brovold, FN 1968, State of the art: Effect of water on bitumen aggregate mixtures: Special HRB Report 98, Highway Research Board: Washington, DC.

Marek, CR & Herrin, M 1968, ‘Tensile behavior and failure characteristics of asphalt cements in thin films’, Journal of the Association of Asphalt Paving Technologists, vol. 37, pp. 386-421.

Masad, E, Zollinger, C, Bulut, R, Little, D & Lytton, R 2006, T Characterisation of HMA moisture-damage using surface energy and fracture properties’, Journal of the Association of Asphalt Paving Technologists, vol. 75, pp. 713-754.

Miller, JS & Bellinger, WY 2003, Distress identification manual for the long-term pavement performance program: FHWA-RD-03-031, Office of Infrastructure Research and Development FHWA: McLean, Virginia.

Mortazavi, Massoud, and James S. Moulthrop. "The SHRP materials reference library." (1993).

Moore, DR & Williams, JG 2001, ‘Peel testing of flexible laminates’, in DR moore, A Pavan & JG Williams (eds), Fracture mechanics testing methods for polymers adhesives and composites: ESIS Publication 28, Elsevier: Oxford, United Kingdom, pp. 203-224.

Moore, DR 2008, ‘An introduction to the special issue on peel testing’, International Journal of Adhesion and Adhesives, vol. 28, pp. 153-157.

Moyassari, A., Gkourmpis, T., Hedenqvist, M., & Gedde, U. (2019). Molecular Dynamics Simulations of Short-Chain Branched Bimodal Polyethylene: Topological Characteristics and Mechanical Behavior. *Macromolecules*, *52*(3), 807-818. doi: 10.1021/acs.macromol.8b01874

Mullins, Oliver C. "The modified Yen model." Energy & Fuels 24, no. 4 (2010): 2179- 2207.

Murgich, Juan, Jesús Rodríguez, and Yosslen Aray. "Molecular recognition and molecular mechanics of micelles of some model asphaltenes and resins." Energy & Fuels 10, no. 1 (1996): 68-76.

Miller, C., Little, D. N., Bhasin, A., Gardner, N., & Herbert, B. (2012). Surface energy characteristics and impact of natural minerals on aggregate–bitumen bond strengths and asphalt mixture durability. Transportation Research Record: Journal of the Transportation Research Board, 2267(1), 45–55. https://doi.org/10.3141/2267-05

Mirzababaei, P. (2016). Effect of zycotherm on moisture susceptibility of warm mix asphalt mixtures prepared with different aggregate types and gradations. Construction and Building Materials, 116, 403–412. https://doi.org/10.1016/j. conbuildmat.2016.04.143

NCAT, NCAT Researchers Explore Multiple Uses of Rejuvenators. 2014, National Center for Asphalt Technology. p. 7-9.

Nkanga, U., Joseph, J., Adams, F., & Uche, O. (2017). Characterization of Bitumen/Plastic Blends for Flexible Pavement Application. Procedia Manufacturing, 7, 490-496. doi: 10.1016/j.promfg.2016.12.051

NTEC 2007, Tensile Bond Testing (TBT): Laboratory Operations Procedures-Test Methods/Testing, LOP 9.28, Nottingham Transportation Engineering Centre: University of Nottingham, Nottingham.

Nosé, S. (1984). A unified formulation of the constant temperature molecular dynamics methods. The Journal Of Chemical Physics, 81(1), 511-519. doi: 10.1063/1.447334

Pahlavan, Farideh, Masoumeh Mousavi, Albert Hung, and Ellie H. Fini. "Investigating molecular interactions and surface morphology of wax-doped asphaltenes." Physical Chemistry Chemical Physics 18, no. 13 (2016): 8840-8854.

Pan, Tongyan, Yang Lu, and Stephen Lloyd. "Quantum-chemistry study of asphalt oxidative aging: an XPS-aided analysis." Industrial & Engineering Chemistry Research 51, no. 23 (2012a): 7957-7966.

Pan ,Tongyan, Yang Lu, and Zhaoyang Wang. "Development of an atomistic-based chemophysical environment for modelling asphalt oxidation." Polymer degradation and stability 97, no. 11 (2012b): 2331-2339.

Pan, Jielin, and Rafiqul A. Tarefder. "Investigation of asphalt aging behaviour due to oxidation using molecular dynamics simulation." Molecular Simulation 42, no. 8 (2016): 667-678.

Pan, J., Hossain, M. I., & Tarefder, R. A. (2017). Temperature and moisture impact on asphalt before and after oxidative aging using molecular dynamics simulations. Journal of Nanomechanics and Micromechanics, 7(4), 04017018. https://doi.org/10.1061/(ASCE)NM.2153-5477.0000139

Pan, J., & Tarefder, R. A. (2016). Investigation of asphalt aging behaviour due to oxidation using molecular dynamics simulation. Molecular Simulation, 42(8), 667–678. https://doi.org/10.1080/08927022.2015.1073851 \

Pavement Interactive n.d., Moisture susceptibility, retrieved June 25, 2008, from http://pavementinteractive.org/index.php?title=Moisture_Susceptibility

Paul T. Williams, Elizabeth A. Williams, Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock, J. Anal. Appl. Pyrolysis 51 (1999) 107–126.

Petersen, J. C., F. A. Barbour, and S. M. Dorrence. Catalysis of Asphalt Oxidation by Mineral Aggregate Surfaces and Asphalt Components. Proc., Association of Asphalt Paving Technologists, Vol. 43, 1974, pp. 162–177

Petersen, J. C. "Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art." Transportation Research Record 999: 13 (1984).

Petersen, J. Claine. "Quantitative functional group analysis of asphalts using differential infrared spectrometry and selective chemical reactions--theory and application." Transportation Research Record 1096 (1986).

Petersen, J. C., R. E. Robertson, J. F. Branthaver, P. M. Harnsberger, J. J. Duvall, S. S. Kim, D. A. Anderson, D. W. Christiansen, and H. U. Bahia. "Binder characterization and evaluation: Volume 1." Rep. No. SHRP-A-367, Strategic Highway Research Program, National Research Council, Washington, DC., Google Scholar (1994).

Petersen, J. Claine. "A review of the fundamentals of asphalt oxidation: chemical, physicochemical, physical property, and durability relationships." Transportation Research E-Circular E-C140 (2009).

Petersen, J. Claine, and Ronald Glaser. "Asphalt oxidation mechanisms and the role of oxidation products on age hardening revisited." Road Materials and Pavement Design 12, no. 4 (2011): 795-819.

Petersen, J. C., & Glaser, R. (2011). Asphalt oxidation mechanisms and the role of oxidation products on age hardening revisited. Road Materials and Pavement Design, 12(4), 795–819. https://doi.org/10.1080/14680629.2011.9713895

Pérez-Lepe, Antonio & Martínez Boza, Francisco & Gallegos, C. (2005). Influence of Polymer Concentration on the Microstructure and Rheological Properties of High-Density Polyethylene (HDPE)-Modified Bitumen. Energy & Fuels.

Rahman, M. (2004). Characterisation Of Dry Process Crumb Rubber Modified Asphalt Mixtures. *University of Nottingham School Of Civil Engineering*.

Rand. DA 2002, 'HMA Moisture Sensitivity, Past, Present & Future, TxDOT Experiences', paper presented to the Session 3 Field Observations and Validation, Designed Test and Forensic Analysis of the 39th Moisture Damage Symposium, Wyoming, July 15-17, 2002.

Rakesh, L., Modeling and Bio molecular Self-assembly via Molecular Dynamics and Dissipative Particle Dynamics. Numerical Analysis and Applied Mathematics, Vols 1 and 2,2009. 1168: p. 832-835

Read, J., & Whiteoak, D. (2003). *The Shell Bitumen Handbook*, (5th ed.).

Reinke, G., and S. Glidden. Determination of Phosphorus in Asphalt Binders and in Binders Recovered from Bituminous Mixtures. Presented at Petersen Asphalt Research Conference, Laramie, Wyo., June 16–18, 2002.

Reinke, G., and S. Glidden. Determination of Phosphorus in Asphalt Binders and in Binders Recovered from Bituminous Mixtures. Presented at North East Asphalt User/Producer Group Meeting, 2007.

Robertson RE. Chemical properties of asphalts and their relationship to pavement performance. In: Strategic highway research program. Washington, DC, USA: National Research Council; 1991.

Rice, JM 1959, 'Relationship of aggregate characteristics to the effect of water on paving mixtures', in Symposium on Effect of Water on Bituminous Paving Mixtures: ASTM Special Technical Publication

No. 240, Boston, Massachusetts, June 24, 1958, American Society for Testing and Materials: Philadelphia, pp. 17-34.

Sudip Kumar Sen, Sangeeta Raut, Microbial degradation of low- density polyethylene (LDPE): A review, Journal of Environmental Chemical Engineering, Volume 3, Issue 1, 2015, Pages 462-473, ISSN 2213-3437.

Sun, B., Lu, L., & Zhu, Y. (2019). Molecular Dynamics Simulation on the Diffusion of Flavor, O2 and H2O Molecules in LDPE Film. *Materials*, *12*(21), 3515.

Takanohashi, Toshimasa, Shinya Sato, Ikuo Saito, and Ryuzo Tanaka. "Molecular dynamics simulation of the heat-induced relaxation of asphaltene aggregates." Energy & fuels 17, no. 1 (2003): 135-139.

Tarrar, AR & Wagh, VP 1992, The effect of the physical and chemical characteristics of the aggregate on bonding: Strategic Highway Research Program Report AUIR-91-507, National Research Council: Washington DC.

Taylor, A 1996, Impact testing of adhesive joints: MTS Adhesives Project 2 Failure Modes and Criteria Report No. 5 Annex 2, Imperial College of Science, Technology and Medicines: London, United Kingdom.

Taylor, MA & Khosla, NP 1983, 'Stripping of asphalt pavement: State of the art',Transportation Research Record, vol. 911, pp. 150-157.

Tandon, V & Puentes, I 2006, 'Development of portable device to measure tack coat quality in the field', Proceedings of the 2006 Airfield and Highway Pavement Specialty Conference, Atlanta, Georgia, April 30-May 3,2006, America Society of Civil Engineers: Atlanta, Georgia, pp. 589-600.

Terrel, RL & Al-Swailmi, S 1994, Water sensitivity of asphalt-aggregate mixes: Test selection: Strategic Highway Research Program Report A-403, Oregon State University: Corvallis, Oregon.

Xu, G., & Wang, H. (2016). Study of cohesion and adhesion properties of asphalt concrete with molecular dynamics simulation. Computational Materials Science, 112, 161–169. https://doi.org/10.1016/j.commatsci.2015.10.024

Xu, G., & Wang, H. (2017). Molecular dynamics study of oxidative aging effect on asphalt binder properties. Fuel, 188, 1–10. https://doi.org/10.1016/j.fuel.2016.10.021

Uddin, W., Kanok Boriboonsomsin, and Sergio Garza. Transportation Related Additional Low-density Polyethylene Impacts and Societal Costs For Life-Cycle Analysis of Costs and Benefits. IJP – International Journal of Pavements, Vol. 4, No. 1-2, January-May 2004, pp. 92-104.

Vargas, M., Vargas, M., Sánchez-Sólis, A., & Manero, O. (2013). Asphalt/polyethylene blends: Rheological properties, microstructure and viscosity modeling. *Construction And Building Materials*, *45*, 243-250.

Van Gunsteren, W. (2019). Book Reviews: Molecular Dynamics Simulation. Elementary Methods. By J. M. Haile. Angewandte Chemie International Edition In English, 32(5), 765-765.

Vasudevan R., Nigam S.K., Velkennedy R., Ramalinga Chandra Sekar A., Sundarakannan B. Utilization of Waste Polymers for Flexible Pavement and Easy Disposal of Waste Polymers, International Conference on Sustainable Solid Waste Management, 5 - 7, Chennai, India pp-105-111, 2007.

Wignall, A, Kendrick, PS & Ancill, R 1991, Roadwork-Theory and practice, 3rd edn, BH Newnes: Oxford, UK.

Wood, PR 1958, 'Rheology of asphalts and the relation to behavior of paving mixtures', Highway Research Board, Bulletin 192, p. 20.

Wu, Z & Hossain, M 2003, Pilot instrumentation of a Superpave test section at the Kansas accelerated testing laboratory: KSU-98-2, Kansas State University: Manhattan.

Yao, Hui, Qingli Dai, and Zhanping You. "Molecular dynamics simulation of physicochemical properties of the asphalt model." Fuel 164 (2016): 83-93.

Yoon, HH & Tarrar, A 1988, 'Effect of aggregate properties on stripping', Transportation Research Record, vol. 1171, pp. 37-43.

Zhang,C 2005, 'Comparative study of the physical and mechanistic properties of HMA mixture: Filed vs Laboratory', MSc Thesis Louisiana State University, Louisiana, retrieved November 16, 2008, from http://etd.lsu.edu/docs/available/etd-04132005-144806/unrestricted/Zhang_thesis.pdf.

Zhang, Liqun, and Michael L. Greenfield. "Analyzing properties of model asphalts using molecular simulation." Energy & fuels 21, no. 3 (2007): 1712-1716.

Zoorob, S., & Suparma, L. (2000). Laboratory design and investigation of the properties of continuously graded Asphaltic concrete containing recycled plastics aggregate replacement (Plastiphalt). *Cement And Concrete Composites*, *22*(4), 233-242. doi: 10.1016/s0958-9465(00)000263

Zhang, X., Li, Z., Lu, Z., & Sun, C. (2002). The crystallization of low-density polyethylene: a molecular dynamics simulation. *Polymer*, *43*(11), 3223-3227. doi: 10.1016/s0032-3861(02)00126-x